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TRANSLATION

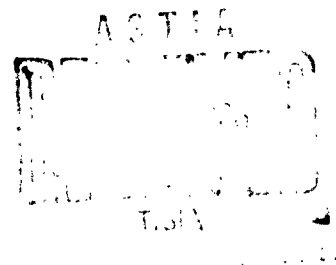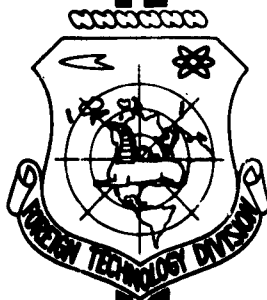REACTIONS IN MIXTURES OF SOLIDS

BY

P. P. Budnikov and A. M. Gnistling

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REACTIONS IN MIXTURES OF SOLIDS

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The present monograph illuminates the theory, methods of study, and range of application of reactions in mixtures of solid substances, which form the basis for preparation of many important structural and various other types of materials.

In addition to describing the structure and physicochemical properties of crystalline bodies and their behavior on heating, which is associated, among other things, with processes of diffusion, sintering, recrystallization, fusion, sublimation and polymorphic transformations, the book examines the mechanism, thermodynamics, kinetics, classification principles, and methods of controlling the rate of chemical reactions in solids. The results of numerous investigations of the processes in which spinelides, titanates, zirconates, silicates and other technically important compounds are formed by reactions in crystalline mixtures are presented.

The applications of the above reactions in the technology of adhesives, refractory materials, and ceramic products are examined. Certain basic problems and study trends for reactions in solids are examined in the light of the most important problems of the country's technical progress.

The book is intended for engineering-technical and scientific workers in the structural-materials industry and related branches of engineering.

TABLE OF CONTENTS

FOREWORD

Implementation of the grandiose tasks placed before the country by the 21st Congress of the CPSU requires further balanced development of theoretical and applied research in various fields of knowledge and universal mobilization of the attainments of science for their exploitation in industry.

The chemistry of solids is one of the most important branches of modern science. The importance of knowledge concerning reactions in mixtures of crystalline solids from the standpoint of the structural-materials, metallurgical, and chemical industries and certain other important branches of technology is a familiar fact at the present time. This science, which emerged in its original form at the beginning of the nineteen-twenties, i.e., over 30 years ago, has undergone continuous development. At the present time, it is based to a considerable degree on the attainments of theoretical and experimental physics and physical chemistry, which have made it possible to account for and describe many phenomena that take place on heating of crystalline solids.

In the course of several decades of work by numerous investigators, abundant experimental material on reactions in mixtures of crystalline solids has been accumulated.

There is no doubt of the necessity of elucidating a theory of these reactions and generalizing at least the most important experimental data on them. At the same time, our literature is gravely deficient in this field. As we know, only a single relatively short mono-

graph on reactions in solids has been published in the USSR; this was
written by one of the authors in collaboration with A.S. Berezhnoy [1]
over 10 years ago. The present monograph represents an attempt to fill
this gap.

At the contemporary level of knowledge in the field of interest
to the authors and the present tempo of its development, this mono-
graph can have no pretense to exhaustive examination of all or even
all of the basic problems of solid-state chemistry. The authors have
set themselves the much more modest goal of devoting brief considera-
tion to the most important problems in this field of science.

Not all of the aspects of reactions in mixtures of solids have
been studied with uniform thoroughness; certain results of work by
various investigators are contradictory; the basic premises cannot
even be regarded as definitively established. As regards these points,
it has been necessary for us to restrict ourselves to indicating the
doubtfulness of the corresponding data or to formulating problems for
further research.

The reactions to be considered in the material that follows and
the substances obtained by them are of great technological importance.
Study of some of them is of considerable theoretical interest in that
it opens possibilities for generalizations in the field, for example,
of the reaction mechanism in solids. Other reactions enable us to pro-
duce new products, investigation of whose properties may lead to their
extensive technical utilization (as was the case recently in connection
with, for example, a number of iron, titanium, zirconium, beryllium
and uranium compounds). The present monograph devotes specific atten-
tion to different reactions.

The authors feel themselves obliged to express their profound
gratitude to N.A. Toropov, V.P. Barzakovskiy and A.D. Volkov for their

valuable advice and commentaries.

Naturally, the work being presented to the reader is not free of defects; the authors will accept notification of these with gratitude.

INTRODUCTION

Recently, a relatively young branch of science concerned with study of chemical reactions in solids has been acquiring increasing importance. In the contemporary literature, this division is known under the name of solid-state chemistry, a phrase proposed as long ago as 1902 by F.M. Flavitskiy [2].

This lumping together of reactions in solids having the most diverse chemical compositions and properties, which will seem somewhat strange to the inorganic chemist and is not justified by the old classical chemistry is the result of at least two causes.

The first of these reasons (which is of a purely historical nature) consists in the fact that reactions of this type were avoided by science for a very long time: as we know, the conviction that solids do not, as a rule, react with one another was widely held up to the beginning of the XIX century. Study of the so-called solid-phase reactions was begun much later than that of reactions in gases and liquids. As a result, information concerning reactions in solids came to form, as it were, an independent region of chemistry which has developed to a certain degree in isolation from its other regions.

A second factor that has resulted in unification of these reactions into a large common group consists in their specific nature, which differs in many respects from that of reactions in gases and liquids. The fact is that when crystalline solids interact, it is in practice almost impossible for an independent chemical event to occur between them. It is inevitably accompanied (and frequently preceded) by

the various physical and physicochemical processes that are intimately related to it, without understanding and study of whose laws it is impossible not only to manipulate the reactions deliberately, but sometimes even to visualize the course that they take. Certain processes in solids represent intimately interwoven physical and chemical phenomena. This is the reason for the enormously important role taken by physics and physical chemistry in the study of reactions in solids.

At the present time, it is well known that ideal solid bodies do not exist in practice, in exactly the same way as there are no ideal liquids and gases. However, while the difference between real and ideal liquids and gases has been extensively used for a long time by technology for the most diversified purposes, researchers and engineers have been concerned only during the last 20-30 years with systematic study of the deviations of real crystalline bodies from ideal bodies and, in particular, artificial creation of various types of deviations in the crystal lattice with the object of making practical use of them. As an example, the so-called defect chemistry of crystals and the theory and technology of fabricating semiconductor materials underwent serious development only during the last 10-15 years. To this we should add that the defects mentioned here are distinguished by wide variety, while the characteristics of the solid that are associated with them are sometimes of high complexity. Together with the above-noted variety of processes that accompany reactions in solids, this also makes its imprint on the chemistry of solids. As a result, this field still has many unresolved problems of a theoretical and practical nature.

Hardly the least of these is scientific description of the essential nature and mechanism of the phenomena that accompany this kind of reaction and methods of exercising deliberate control over these phenomena with the objective of rigorous regulation of both their direction

and their rate, as well as the properties of the products obtained. Solution of this problem naturally requires a conception of the conditions under which reactions take place in solids. Usually, these reactions occur in mixtures of powders, i.e., solids with imperfect contact between their grains. The spaces between the grains are filled with a fluid or gas which, together with the granules of the crystalline reagents, forms a definite physical background against which the reaction takes place. During accomplishment of the reaction, mass transfer takes place between the phases, possibly with participation of all of the phases present. Among other things, external diffusion of matter between granules may take place in addition to internal, intercrystalline diffusion. Consequently, without concerning ourselves here with the relative importance of either, we may note that in the general case, study of intercrystalline diffusion is inadequate to describe the mass-transfer process and, accordingly, the reaction mechanism in the powder mixture. This will require thorough analysis of the parts played by all phases in the reaction. The practical importance of the reactions to be described, the complexity of describing the relationships that they embody, and the urgency of the technical problems connected with them have made them the object of persistent research over the course of many years.

When, after the familiar discoveries of Anosov (1837), Beketov (1859) and Chernov (1877) in the field of reactions between solids and the experimental research of Spring (1885-1888) in this field, the First Mendeleyev Congress in 1907 discussed a report by Flavitskiy entitled 'Basic methods and reactions in solid-state chemistry", and even when, in the nineteen-twenties, the famous investigators Tammann and Hedwal published their series of monumental reports on reactions of this type, it would have been difficult to predict that they would

- 6 -

become a major and important branch of chemical engineering and form a basis for many important industrial processes.

At the present time, solid-state chemistry forms a respectable branch of science that is important for the technology of silicates, metallurgy, the technology of the basic chemical industry, and many other branches of contemporary engineering.

Many highly important industrial processes are accomplished by or with participation of reactions in solid mixtures. To evaluate the importance of these processes to the national economy, it is sufficient to note that they include reduction of iron ores in the production of cast iron, the formation of cementite clinker, refractory materials and ceramic products, caustic soda and certain mineral salts, as well as roasting of sulfide ores, agglomeration of the charges in the production of alumina, etc. An enormous number of reactions in mixtures of solids have been reported. These include reactions of oxides, metals and sulfates with carbon, metals, and sulfides, the production of silicates, ferrites, aluminoferrites, titanates, and other compounds from oxides, reactions between various salts in crystalline mixtures, and many others.

Researchers in various countries, notably Bulgaria, Germany, the Soviet Union, the USA, France, Czechoslovakia, Sweden, and Japan, have been attacking study of these reactions persistently and successfully over the course of the last several decades.

In the postwar years, over a thousand papers devoted to individual investigations have been published, together with several generalizing monographs concerned directly with reactions between solids. Several major conferences and international congresses have been held over the last few years to consider problems of reactions in solids. These have aroused tremendous interest in scientific and industrial circles.

Following publication of the reports of Flavitskiy (1902-1907), Cobb (1909) and Hedwal (1911-1914), which established the basic possibility and nature of many reactions in crystalline mixtures, the investigations of Tammann, Hedwal and their school in 1922-1924 laid the foundations for systematic study of these reactions.

The original goal of these researchers consisted in ascertaining the direction and specific properties of the various types of reactions between solids, the influence exerted upon them by temperature, agitation, and certain other factors. The success of this approach was not limited simply to the establishment of certain particular relationships and general qualitative laws governing the so-called solid-phase reactions. The high technical importance of many of them was also ascertained and various methods were developed for their experimental investigation, leading to the next stage in the development of research in this field. This stage, which is approximately associated with the nineteen-thirties, is characterized by the broad scope of the experimental work done and, accordingly, by the accumulation of a large quantity of experimental data concerning the influence of granulometric and chemical composition of the reaction mixtures, the influence of impurities, pressure, gaseous-phase composition, and many other conditions of the process on various reactions between solid substances. The establishment of empirical relationships concerning the questions listed above and certain others was particularly necessary in connection with their importance for the technology of silicates and for metallurgy. These years saw circumstantial research into the reactions which result in formation of Portland-cement-clinker minerals, alumina cement, various refractory materials and glasses, the reduction processes of certain crystalline oxides, roasting of certain nonferrous and ferrous-metal ores, and the preparation of soluble com-

pounds of aluminum, chromium and a number of other elements. Optimum compositions of the initial crystalline mixtures were established, together with the necessary conditions for their high-temperature processing for applications in technological processes of various branches of industry.

The postwar years witnessed particularly profound study of the theory of reactions in crystalline mixtures. Efforts toward deliberate control of these reactions under complex industrial conditions, toward rigorous purposive regulation of these conditions, and toward radical increases in the rates of reactions in crystalline mixtures and a considerable improvement in the quality of the resulting products led to circumstantial study of their mechanisms, thermodynamic characteristics, kinetics, and intensification factors.

Systematic research in this field is being prosecuted successfully by investigators in a number of countries, and in the Soviet Union and Sweden in particular. The progress made in these projects has made an important contribution to extensive development of a theory of solids (particularly crystal chemistry and the theory of diffusion in solids) and a theory of heterogeneous physicochemical processes (in particular, chemical kinetics) toward the nineteen-forties. In addition, the relatively widespread use of new methods of experimental research (radioactive isotopes, improved thermal and dilatometric analyses, electron-microscope research, x-ray ionization analysis, and so forth) by the nineteen-forties opened major possibilities in the field of study of processes in solids. Modern science is exploiting these possibilities with even greater energy in view of the fact that there are still many points to be researched in the area of processes of this type.

Chapter 1

THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF SOLIDS

§1. THE CRYSTALLINE STATE OF MATTER

As we know, bodies having a crystalline structure whose laws and nature determine their properties to a considerable degree are known as solids. It is therefore appropriate to preface our elucidation of problems relating to reactions in solid mixtures with a brief exposition of contemporary conceptions of the crystalline state of matter.

The particles of matter in the crystalline state have a stable symmetrical arrangement, forming a crystal space lattice. The structure of the lattice, which is readily established at the present time by x-ray techniques, is intimately related to the chemical structure of the material in the majority of cases.

As was shown as long ago as 1890 by the noted crystallographer Fedorov [3], this relationship can be observed even in crystals, although in a somewhat less distinct form. Normally, the more stable the chemical composition of the body, the higher will be the degree of symmetry observed in its crystal. For example, 50% of the elements and about 70% of the binary compounds form cubic crystals, 75 to 85% of compounds with four to five atoms in the molecule form hexagonal and rhombic crystals, and about 80% of the complex organic compounds form rhombic and monoclinic crystals. This situation is accounted for by the fact that the more uniform the component parts of the crystal lattice, the more ordered is the arrangement that they assume in space.

Another interesting relationship characteristic of the link be-

tween the structure of a crystal and its chemical composition is the fact that structurally analogous molecules of matter (e.g., $BaSO_4$, $PbSO_4$, $SrSO_4$ or $CaCO_3$, $MgCO_3$, $FeCO_3$, $MnCO_3$, $ZnCO_3$) crystalline in similar crystalline forms. The similarity of the crystal lattices of the isomorphic series of substances formed in this manner corresponds to the similarity of their crystals.

An important special property of the crystalline state of matter is its anisotropy, which consists in differences in the physical properties of a chemically homogeneous crystal in its different directions. Anisotropy may be observed in the mechanical, optical, diffusion, thermal and electrical properties of crystalline bodies. Among other things, it is manifested in different rates of crystal growth in different directions, with the result that some of the crystal faces are developed to higher degrees than others.
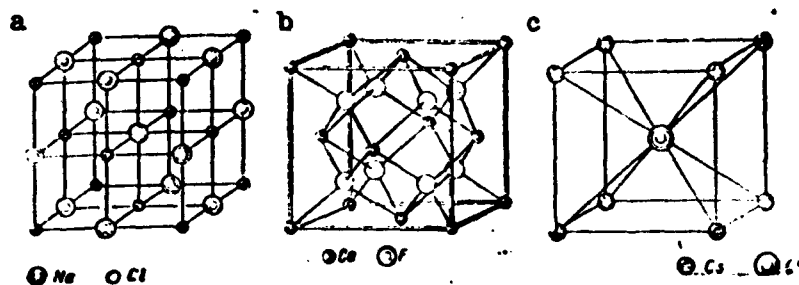
Fig. 1. Ionic lattices. a) NaCl; b) CaF_2; c) C_8Cl.
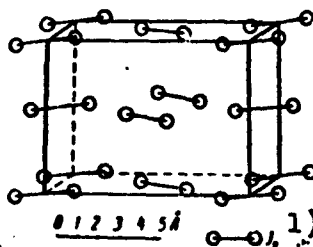
Fig. 2. Molecular lattice (iodine): 1) I_2.

- 11 -
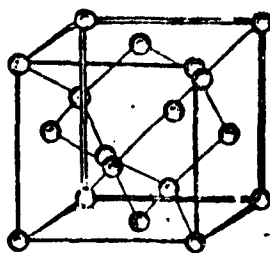
Fig. 3. Atomic lattice (dia-
mond).
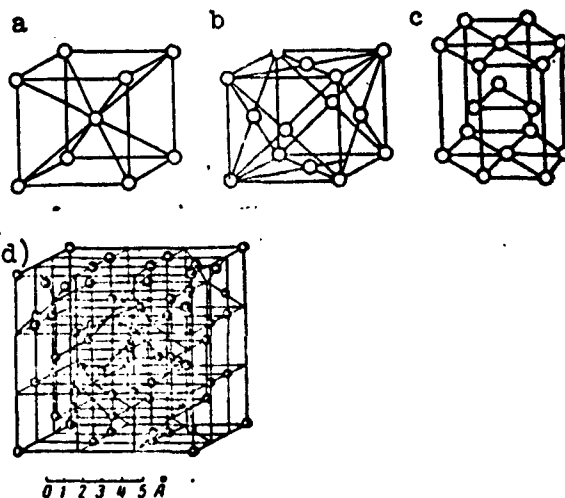
Fig. 4. Metallic lattices. a) Body-centered
cubic (K, Na, Ba); b) face-centered cubic
(Cu, Ag, Au); c) hexagonal compact (Be, Mg,
Zn, Cd); d) complex cubic (α-Mn).

The structural elements forming the crystal and the interaction

forces between them may be of various types. In accordance with this,

we distinguish ionic, molecular, atomic and metallic lattices. Lat-

tices of various intermediate types are also quite commonly encoun-

tered in practice. It has been established by research that the bond

in the lattices of many crystalline compounds is an intermediate form

and that the types of the various bonds in a compound formed from

three or more chemical elements are frequently of different types.

They are said to be ionic, atomic, etc. in accordance with the nature

- 12 -

of their predominating bonding forces.

In the ionic or heteropolar lattice that is characteristic for the majority of salts and typical for inorganic compounds, the forces of interaction between its structural elements are basically electrostatic. Such a lattice forms a regular alternation of oppositely charged ions (Fig. 1) that are linked with one another by the electrical attractive forces of the various charges.

In a molecular lattice — that formed by molecules (Fig. 2) — the interaction between the molecules is effected by dipolar (between asymmetrical polar molecules) and polarization (between symmetrical nonpolar molecules) van der Waals forces, which are considerably weaker than the forces of the intramolecular covalent bonds and the electrostatic forces (the van der Waals dipolar bonding forces are particularly small).

Crystalline H_2, N_2, O_2, I_2, CO_2, H_2O and numerous organic compounds have such a structure.

In the atomic or homeopolar lattice (Fig. 3) that is characteristic for many nonmetals, all of the atoms composing the lattice are neutral and linked to one another by covalent bonds; their nature is fully accounted for by quantum mechanics [4-7]. The homeopolar bond produces a so-called directional valency: under its influence, the atoms are not only established at definite distances from one another, but also form definite spatial configurations. According to contemporary conceptions, the metallic lattice (Fig. 4) is formed by neutral atoms and positive ions, among which free electrons (the so-called "electron gas") move. Since none of the structural elements in the crystal lattice of a metal has a preferential bond to any other element, such a crystal may, in its entirety, be regarded as a single gigantic molecule.

Let us turn to the structure of the ionic lattice. Since the forces of mutual attraction (and repulsion) of the ions are normally characterized by spherical symmetry, the ions of charges of opposite sign will behave in somewhat the same way as hard spheres that are attracted to one another. In view of this, it is customary to treat ions in first approximation as spherical. The lattice structure is determined primarily by the nature of the compound (AB, AB_2, A_2B_3), i.e., by the number of charges and the distances separating them, as well as by the relationship between the radii of the ions forming the lattice. The chemical nature of the ions is not reflected in the lattice structure, so that chemically similar compounds may ha·   · similar or completely different lattices.

TABLE 1
Ionic Radii (A)*

1 Ионы	2 Заряд иона							
	1+	2+	3+	4+	1-	2-	3-	4-
3 Положительные	Li 0,68 Na 0,98 K 1,33 Rb 1,49 Cs 1,65 Cu 0,96 Ag 1,13 Au 1,37	Be 0,34 Mg 0,74 Ca 1,04 Sr 1,20 Ba 1,38 Zn 0,83 Cd 0,99 Hg 1,12 Cu 0,80 Sn 1,02 Pb 1,26 Mn 0,91 Ni 0,74 Co 0,78 Fe 0,80	B 0,20 Al 0,57 In 0,92 Tl 1,05 La 1,04 Cr 0,64 Fe 0,67 As 0,69 Sb 0,90	C 0,15 Si 0,39 Ti 0,64 Zr 0,82 Th 0,95 Ge 0,44 Sn 0,67 Pb 0,76 Mn 0,52 V 0,61 Mo 0,68 W 0,68 U 0,89				
4 Отрицательные					F 1,33 Cl 1,81 Br 1,96 J 2,20	O 1,36 Se 1,93 S 1,82 Te 2,11	N 1,48 P 1,86 As 1,91 Sb 2,18	C 2,60 Si 2,71 Ge 2,72 Sn 2,94

*After Belov [11] and Bokiy [8]: with refinements to the original values of Goldschmidt [9] and the later values of Pauling [10], proceeding from $r_{0-2} = 1.36$ and new data on the structures of binary compounds.
1) Ion; 2) charge on ion; 3) positive; 4) negative; 5) I.

- 14 -

TABLE 2

Coordination Numbers of Lattice Elements

Ratio of radii of lattice elements $r_A : r_B$	Coordination number	Lattice configuration	Example of lattice
0.155 to 0.225	3	Hexagonal	Boron nitride
0.225 to 0.414	4	Tetrahedral	Zincblende
0.414 to 0.732	6	Octahedral	Rock salt
0.732 to 1	8	Centered cubic	Cesium chloride
~1	12	Face-centered cubic or hexagonal contact	Aluminum, copper

Strictly speaking, ions do not, according to quantum-mechanical conceptions [4-7], have definite radii. By the terms radius and effective radius of an ion in a lattice, we imply the smallest distance to which two like ions can approach one another; closer juxtaposition is opposed by the repulsive forces, which predominate over the attractive forces at short distances when the electron shells come into contact.

In the formation of a lattice, the ions tend to form the most stable possible configuration for it, which corresponds to the free-energy minimum. This corresponds to the shortest possible distance between unlike ions and the largest possible distance between like ions.

The sum of the radii of two unlike ions in a lattice is the distance at which the repulsive forces of the electron shells offset the attractive force of differently charged ionic centers. The attraction of electrons in an ionic crystal toward the centers of positive ions and their repulsion from the centers of negative ions result in considerable deformation of the electron shells. Positive and negative ions of the same electron configuration possess different sizes in a crystal: the anions are considerably larger than the cations.

Naturally, the numerical values of the effective radii of different atoms will be different (Table 1).

Different configurations of the lattice are stable for different values of the radius ratio of the ions forming the lattice. The values of these ratios have been established by simple geometrical juxtapositions of the type that is quite familiar to the crystallographer [11, 12]. Thus, we know that with ratios between ionic radii of ~1; 0.732 to 0.414; 0.414 to 0.225 and <0.225 in the case of a compound of type AB, the respective stable lattices are the close-packed hexagonal and cubic, the cubic (centered cube), octahedral, tetrahedral and hexagonal (see Table 2).

An important characteristic of the crystal lattice is the coordination number of its ion or the coordination numbers of the elements forming it, whether ions, atoms, or molecules.

The coordination number of an ion is the number of adjacent (nearest) oppositely charged ions that surround it symmetrically. This number, which is governed by the ratio between the radii of the ions forming the lattice may be the same (see Fig. 1a) or different (see Fig. 1b) for different ions of the lattice.

The lattice-element coordination numbers corresponding to different values of the radius ratio are listed in Table 2.

The ionic radii depend to a considerable degree on the type of coordination of the lattice that they form. It should be noted in this connection that the radius values listed in Table 1 refer to a coordination number of 6. If the distance A-X between unlike ions with this coordination number is taken as unity, the values of the distance A-X for coordination numbers of 4, 8, and 12 will be 0.94, 1.03, and 1.12, respectively.

§2. STRENGTH OF LATTICE. SURFACE ENERGY OF SOLIDS

In recent years, investigators have quite properly devoted serious attention to the problem of crystal-lattice strength. Study of this

factor makes it possible to understand the nature of the highly important relationships that characterize certain mechanical, thermal and other properties of solids.

The strength and stability of a crystal lattice depend on the forces of interaction between the ions, atoms or molecules forming it.

Let us consider the forces operating in the ionic lattice. The closest neighbors of each ion in this lattice are ions of the opposite charge. As a result, the electrostatic forces of attraction operating between each ion and its neighbors predominate over the repulsive forces. However, certain repulsive forces are also in operation between oppositely charged ions; quantum mechanics [4-7] provides us with an idea of the nature of these forces. Their value, which depends on the distance between the ions, exceeds the value of the electrostatic-attraction forces at short distances.

The crystal-lattice potential energy is the resultant of the attractive and repulsive forces and, in general form, may be expressed by the formula [5]

$$E_p = -\frac{C'}{r^{n_1}} + \frac{C''}{r^{n_2}}.$$ (1)

where the term $-C'/r^{n_1}$ corresponds to the forces of attraction and $+C''/r^{n_2}$ corresponds to the repulsive forces if r is the distance between charges. The values of C' and C'' in this expression depend on the valence of the ions and on certain other factors, while the values of n_1 and n_2 depend on the arrangement of the ions in the crystal and the latter's structure. Normally, the value of n_1 is near 1 in accordance with Coulomb's law, while n_2 lies between the approximate limits 8 and 12.

Thus, the repulsive forces (their absolute magnitudes) diminish more rapidly with increasing distance r than do the attractive forces.

- 17 -

These forces compensate one another at $r = r_0$. It is obvious that in a crystal that is free of external disturbances, the ions must stand at intervals of precisely this distance r_0, which corresponds to equilibrium of the above forces. Here the potential energy of the particles is lowest: the system has its maximum stability.

The variation of the values of these forces as functions of the distance between the elements forming the crystal lattice is represented schematically in Fig. 5.

If one particle of the lattice is situated at the coordinate origin, a second particle will, in accordance with the above, be situated at the point A of intersection of the resultant force with the axis of abscissas in a normal undeformed lattice: here the resultant force is zero and the system is stable. The distance from the coordinate origin to the point A is equal to r_0. Any change in this distance between particles (e.g., as a result of heating of the body*) disturbs the equality of the attractive and repulsive forces and, consequently, raises the potential energy of the system and reduces its stability. The deepest point of a "potential trough" corresponds to the value $r = r_1$, as does the greatest predominance of the attractive forces over the repulsive forces. As $\underline{r}$ is further increased, the excess of the attractive forces diminishes progressively to a negligible value.

The work necessary to rupture the lattice and separate its particles from one another by an infinitely great distance (for practical purposes, by a distance at which the interaction forces between the particles are negligibly small) is known as the lattice energy.

This work depends on the number of structure units in the crystal, their dimensions and valence** and may, according to Kapustinskiy [19] be computed approximately for the ionic lattice from the expression
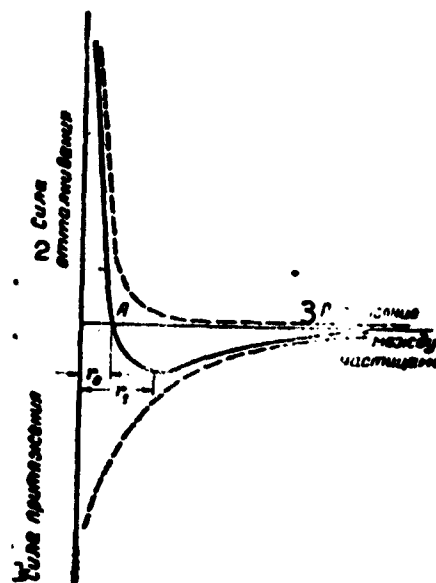
Fig. 5. Attractive and repulsive forces acting in crystalline body as functions of distance between particles. 1) Attractive forces; 2) repulsive forces; 3) distance between particles.

$$U = 256 \frac{z_1 z_2 \Sigma_n}{r_1 + r_2} \quad \text{kcal/g-mol} \tag{2}$$

or, more precisely (taking into account the quantum-mechanical nature of the repulsive forces), from the expression [20]

$$U = 287.2 \frac{z_1 z_2 \Sigma_n}{r_1 + r_2}\left(1 - \frac{\rho}{r_1 + r_2}\right) \text{kcal/g-mol} \tag{3}$$

where Σ_n is the number of ions in the molecule, $r_{1:2}$ and $z_{1:2}$ are the radii (in angstroms for a coordination number of 6) and valences of the cation and anion, and $\rho = 0.345$ is the so-called repulsion coefficient.*

The most important lattice parameters — those determining its energy — are its electronic and nuclear configuration and the values of the ionic potentials.

High energies are inherent to the close-packed, compact lattices

TABLE 3

Hardness of Sulfides of Certain Metals [22]

1 Физико-химическая характеристика	2 Соединения							
	FeS	MgS	CaS	SrS	BaS	ZnS	CdS	HgS
3 Радиус катиона в Å	0,34	0,74	1,01	1,20	1,38	0,83	0,99	1,12
4 Твердость (по Моосу)	7,5	4,5—5	4,0	3,3	3,0	4,0	3,2	3,0
5 Тип решетки . . .	NaCl					ZnS		

1) Physicochemical characteristic; 2) compound; 3) cation radius in A; 4) Mohs hardness; 5) lattice type.

(with large particle coordination numbers) that are formed by ions with high potentials (high ratio of charge to effective radius), which possess stable electron shells.

The lattice energy also determines the hardness of the body to a considerable degree. The stronger the bonding forces between the structural elements, the harder, naturally, will it be, and the more difficult will it be to rupture it.

The data of Table 3 indicate that the hardnesses of different solids possessing lattices of the same type and ions of the same valence are antibatic to the ionic radii.

While similar lattices of different substances are constructed from ions having closely similar sizes, the hardnesses of these substances increase with increasing valence of the ions (Table 4).

The vapor pressure and melting point of the solid naturally depend on the value of the lattice energy: the former diminishes and the latter increases (see §1) with increasing U.

Obviously, substitution of some ion in the lattice by an ion of the same radius but a higher valence or by an ion with the same valence but a smaller radius will result in an increase in the electrostatic

TABLE 4

Hardness of Certain Crystalline Substances [18]

1 Физико-химическая характеристика	2 Соединение							
	CuBr	NaF	MgO	ScN	TiC	LaSe	GaAs	GeAs
3 Межатомное расстояние в Å	2.46	2.31	2 1	2.23	2.23	2.45	2.44	2.43
4 Валентность катионов	1	1	2	3	4	2	3	4
5 Твердость (по Моосу)	2.5	3.2	6.5	7—8	8—9	3—4	4—5	6.5
6 Тип решетки . . .	NaCl				ZnS			

1) Physicochemical characteristic; 2) compound; 3) interatomic distance in A; 4) valence of cations; 5) Mohs hardness; 6) lattice type.

TABLE 5

Melting Points of Certain Substances [18]

1 Физико-химическая характеристика	2 Вещества					3 Соединения			
	Li	Na	K	Rb	Cs	MgO	CaO	SrO	BaO
4 Радиус атома (иона) в Å	1.56	1.92	2.38	2.51	2.70	(0.78)	(1.06)	(1.27)	(1.43)
5 Температура плавления в град......	186	98	63	39	28	2650	2620	2430	1923
6 Тип решетки	CsCl					NaCl			

1) Physicochemical characteristic; 2) substance; 3) compound; 4) radius of atom (or ion) in A; 5) melting point in degrees; 6) lattice type.

attraction, i.e., the lattice energy will rise [see Eq. (3)].

Accordingly, all other conditions the same, such a substitution will result in an increase in hardness (see Table 4) and a rise in the solid's melting point (Table 5), as well as a drop in its vapor pressure.

This means in first approximation that with identical lattice types, we may observe a drop in the hardness and melting point of substances as we move down the columns of the Mendeleyev table, while these properties will rise as we move to the right along the rows of the table.

Examining lattices of various types in the light of the above, it is easy to understand the differences in the physical properties of bodies formed by such lattices.

The electrical bonding energy between ions in ionic lattices and the covalent-bond strength in ionic lattices, which are, in the majority of cases, quite considerable, are responsible for their high compactness and density and, accordingly, for the high melting points and low volatilities of the substances formed by these lattices.

The weakness of the dipolar and polarization van der Waals bonding forces between the elements of molecular lattices (molecules) is responsible for the high volatilities and low melting points of the substances formed by such lattices.

The comparison between the properties of diamond and graphite may serve as a classical illustration of this dependence of the properties of a solid on the nature and strength of the bonds between the elements of its lattice. The covalent bonds between all atoms of diamond give rise to its high hardness and sublimation temperature; graphite, in which the covalent bond exists only in atomic layers (van der Waals bonding forces operate between the layers), is considerably less resistant to mechanical and temperature disturbances.

* * *

Unlike any crystal-lattice structural element (atom, molecule, ion) that is situated in the interior of the body and subject to the forces of the elements surrounding it on all sides, an element (par-

ticle) situated on the surface of a crystalline body interacts only with those particles of the body that lie on this surface and those next to it in the direction of the crystal interior.

Whether in the interior of the body or on its surface, a particle is at rest if the resultant of all the forces is zero. Even with the nonsymmetry of the force field acting on a surface particle, it is in equilibrium because the forces acting on it in the direction of the crystal-phase interior are offset by compression of the surface layer, i.e., by elastic forces.

Thus, the surface layer is in an elastically stressed state. Particles in this layer of a solid possess a larger potential-energy margin than interior particles.

Since the total energy of the crystal, which determines its properties and behavior under various conditions, is composed of its internal and surface energy, it is necessary to devote study to both of these. This is rendered the more important by the fact that the processes of recrystallization, sintering, polymorphic transformation and chemical reaction in crystalline solids normally develop first at the surfaces of their grains and are functions of surface energy and its variations.

For a given volume of a body, its total energy will obviously be the larger the larger its surface area when a given crystalline faceting is retained.

The surface energy is measured in terms of the work necessary to form a surface layer under isothermal conditions. This work, referred to a unit area (to 1 cm^2) of surface is known as the specific surface energy σ and is measured in ergs/cm^2 = dynes/cm.

Strictly speaking, the work of surface formation differs for different particles, i.e., the surface-energy value is not constant for

all points over the surface. However, given an adequate surface area, we may speak of a certain value of σ for a given body as the average energy of formation of a unit of its surface.*

TABLE 6
Surface Energy of Certain Bodies at $0°K$ (ergs·cm^{-2})

1) Поверхностная энергия	2) Соединение			4)				5)
	NaF	NaCl	NaBr	NaJ	KF	KCl	KBr	KI
σ°	171	155	145	132	160	131	124	111
σ(жидк.) 3)	335	190	178	138	212	173	159	139

*The values of σ are given for the (100) faces.
1) Surface energy; 2) compound; 3) liquid; 4) NaI; 5) KI.

Table 6 lists calculated values for the surface energies of crystalline halogen compounds of the alkaki metals at a temperature of $0°K$ and the surface-tension values of the same substances in molten form, as obtained by extrapolation of the experimental values to the same temperature [23, 24].

The numerical value of the specific surface energy depends on the strength of the lattice (bodies with strong lattices are characterized by large values of σ) and, for a given lattice, on the properties of the medium surrounding the body. This last is a result of the fact that the value of σ at the boundary between two phases is determined by the difference in the intensities of the bonding forces between the molecules (atoms,ions) forming these phases. If, for example, the crystal is placed in a liquid that wets it, its surface energy will be reduced as a result of interaction between the surface particles of the crystal and the liquid.

When the temperature of a body is raised, its surface energy, which offsets the bonding forces directed toward the interior of the lattice, is naturally reduced.

A detailed elucidation of these problems is given in the papers by Rebinder, Kuznetsov, and other investigators [25-29].

§ 3. STRUCTURE OF REAL CRYSTALS

Many properties of a real crystalline substance depend on the perfection of its crystal structure. As we know, the chemical activity of real crystals is the higher the greater the difference between their lattice energies and the energies of the ideal crystal lattice (in a perfect crystal lattice, the mass transfer necessary to accomplish a reaction is practically impossible). In view of this, it will be profitable to dwell on the causes, the nature, and the most important consequences of this difference.

The ideal crystal consists of atoms, ions, or molecules regularly arrayed in all directions. Each such crystal has a structural unit or elementary cell that is fully determinate and characteristic for it, and whose exact repetition in each of the three dimensions forms its lattice (see Figs. 1-4).

It has been established by numerous research studies that the structure of real crystals always or almost always differs to one degree or another from this ideally regular structure. This is confirmed experimentally by the presence in real crystals of diffusion, ionic conductivity, scattering of x-ray beams at various angles, and certain other phenomena that are incompatible with the ideal, regular crystal structure. Only in isolated cases has it been possible with great difficulty to produce crystals whose structure approximates the ideal [30-32].

The deviations of the real crystals from ideal crystals take exceedingly diverse forms. The basic deviations or defects, which determine the so-called coarse structure of the crystal, are nonparallelism of its various layers to one another, the inclusion of mother liquor

- 25 -

in the crystal, and "striation" of its faces.

It is easy to envisage the "mosaic" structure of crystals that consist of individual blocks of regular crystal structure that are only slightly rotated with respect to one another (Fig. 6). Such crystals would be grouped among the imperfect* ideal crystals, since the hypothetical structure of the blocks composing them is in itself ideal. In actuality, the dimensions of the blocks usually lie in the range from 10^{-3} to 10^{-6} cm. The angles between the blocks have sizes from fractions of a minute to several minutes. This structure of real crystals has as a consequence that a beam of monochromatic x-rays is reflected by a face of a real crystal not at a certain definite angle (Fig. 7a), as would be the case with an ideal crystal structure, but at various angles (Fig. 7b) differing from one another in some cases by several minutes. The slight disorientation of the real-crystal blocks relative to one another also results in a higher intensity in a ray reflected by the crystal than would be expected on the basis of theoretical calculations.

Fig. 6. Crystal lattice a) of ideal crystal; b) of mosaic crystal.
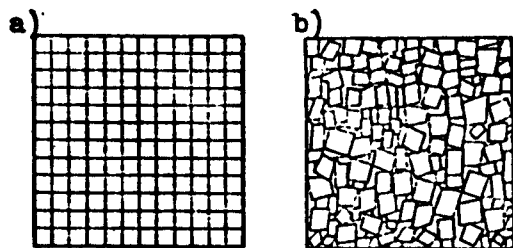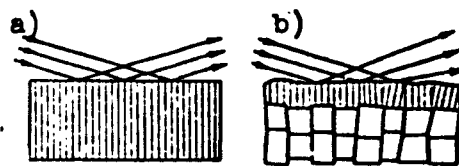
Fig. 7. Reflection of bundle of monochromatic x-rays by face of a) ideal crystal; b) real crystal.

In practice, there are always deviations of one kind or another from the ideal structure in the individual blocks composing the macrocrystal. These deviations, which are known as fine-structural defects, may consist, for example, in the existence of vacancies ("holes")

in the lattice (according to Schottke) or in the presence of so-called dissociated or dislocated displaced atoms occupying lattice points that were hitherto vacant (according to Frenkel). According to Zeyts [Seitz?] [34], we may distinguish six basic types of fine-structural defects: 1) vacancies in the lattice and ions in interstices; 2) foreign ions in the lattice points or in interstices; 3) electrons and "holes"; 4) excitons; 5) dislocations and 6) phonons.

Many investigations have been devoted to study of the structure of real crystals and those of their porperties that are related to the various structural defects. Best-known among these are the studies of Fedorov, Smekal, Tsvikki [Zwicky?], Schottke, Balarev, Frenkel', and Vagner.

In the conception of Fedorov [35], the conditions of crystallization as manifested in its rate exert a profound influence on the coarse structure of a crystal. "Molecular" growth takes place when the crystal develops slowly, while in rapid development growth proceeds by parallel deposition of many minute crystal seeds that arise in the vicinity of the growing surface. This has its effect on the crystal's structure.

Regarding the formation and existence of ideal crystals as possible in principle, Smekal [36] attached great significance to the dependence of the properties of real crystals on their surface defects and devoted much time to their investigation.

The most obvious defects of the crystal are its internal and surface cracks, which are sometimes distinguishable under the microscope or even with the unaided eye. In 1934, Ioffe [37] demonstrated convincingly in experimental research with the example furnished by rock salt that the presence of surface cracks determines the mechanical properties of the crystals (their tensile strength).

According to Smekal, the large cracks mentioned above may be due to tensions governed by primary cracks that have formed under the influence of absorbed impurities or as a result of excessively high crystal growth rates.

On the basis of theoretical analysis, Tsvikki [38] arrived at the conclusion that numerous cracks separated from one another by crystalline blocks about 100 A across must exist on crystal surfaces. These blocks, according to Tsvikki, form a secondary periodic structure or a crystal superlattice that is more stable than the normal nonmosaic structure of the crystal.

Balarev [39] applied thermodynamic analysis to derive the conclusion that the ideal macrocrystal cannot be in equilibrium with its mother liquor. When such a crystal dissolves, it first decays into numerous fine particles (microcrystals) which then exist in solution for a certain time. In the opinion of Balarev, each of the elementary crystals making up the colloidally dispersed macrocrystal contains atoms or ions only in approximately stoichiometric quantities; this circumstance results in an increase in surface activity in the internal walls of fissures or cracks. Thus, according to Balarev, a regular adsorption of ions takes place in the fissures rather than random accumulation of mother liquor.

In actuality, we may speak of nonstoichiometric composition not only as it applies to the elementary crystals.

Defect crystals, which are characterized by an excess or deficiency of one of the components as compared to the stoichiometric composition, are of great importance. The ideal stoichiometric composition of a crystalline compound, on the other hand, is not, generally speaking, absolutely necessary, and is even metastable for certain compounds (e.g., for wuestite). The manner of deviation from

ideal equilibrium chemical composition in such compounds depends on the nature of the excess component and the possible valence states of the anions and cations. The valence of the cation may, for example, drop where there is an excess of metal and rise where there is an excess of nonmetal.

Alkali-halogen compounds, e.g., sodium chloride heated in sodium vapor [33, 40, 41], may serve as the simplest example of substances with this type of defect.

We are indebted for the most part to Shottke and Frenkel for elaboration of our conceptions concerning the fine structure of real crystals.

Shottke postulated the existence of unoccupied points in the lattice of the real crystal. Such defects can occur in the atomic and molecular lattices.

In his monumental works on the theory of liquids and solids [42-45], Frenkel formulated conceptions of the fine structure of the latter and of their behavior under various sets of conditions. Proceeding from these conceptions, which are considered in detail in Chapter 2, we may account for the most important properties of solids. Here it is only necessary to note that ordered state $\rightleftarrows$ disordered state lattice transitions require activation energies, with the left-to-right transition always endothermic.

As in the case of a chemical reaction that takes place with an activation energy, the high-temperature equilibrium may be "frozen" by abrupt cooling of a crystal system having a certain number of fine-structural defects. The result is some irreversibly disturbed system. Since the disorder of the crystal is aggravated as the temperature rises, it may prove sufficiently high on such abrupt cooling ("freezing"); mosaic structure and cracks in real crystals compose the de-

- 29 -

fects of the second type, and the third source and type of [defect] is associated with the presence of impurities in the lattices.

In the field of the structure and the laws governing the property changes of real crystals, there are still many contradictions, differences of opinion, and unclear points.

Critical examination of many studies relating to this field — in particular, those of Balarev and Tsvikki [38, 39] — indicates the unjustified nature of some of their conclusions. However, while they differ in the explanations given for the violation of ideal structure in real crystals, all of the researchers are in agreement on the point that these violations practically always occur for one reason or another and exert significant influence on the properties of solids. Specifically, the following may be causes of the appearance of cracks:

mechanical processing of crystalline solids, e.g., milling;

thermal deformation as a result of abrupt changes in volume on sharp temperature changes;

stresses resulting from polymorphic transformations;

the effects of surface forces;

the formation of vapors and gases in crystals;

recrystallization;

adsorption;

rapid and nonuniform growth of crystals and many other phenomena.

It is generally acknowledged that the formation of ideal or near-ideal crystals involves great difficulties and is possible only in extremely rare exceptional cases with special selection and careful regulation of the crystallization conditions. This viewpoint, which took root long before the appearance of the electron microscope, has been fully confirmed in our time with the aid of electron-microscope

methods of investigation, which, among other things, have made it possible to establish exactly and study in detail the mosaic structure of monocrystals.

It has been established that monocrystals are not, in actuality, fully uniform, but consist of an enormous number of parts in which individual microscopic regions deviate — if ever so slightly — from the average crystallographic directions characteristic of the monocrystal as a whole.

The crystalline solids with which we deal in practice are usually conglomerates composed of a multitude of small crystals that have grown together. In such polycrystalline bodies or crystallites, corresponding crystallographic directions are generally rotated relative to one another through all possible angles. Consequently, crystallites consisting of small microscopic crystals, as, for example, those of ordinary metals, are practically isotropic.

As we know, it is rarely necessary to deal with chemically pure substances under industrial conditions. Chemical engineering, metallurgy, and the technology of silicates are constantly encountering materials whose chemical compositions are nonuniform. In the solid state, they also form fine-crystalline aggregates in which the small crystals may be either uniform or heterogeneous as regards their structure and composition. In the simplest case, each of the system components forms its own crystals, which are chaotically mixed in the crystallite with crystals of another or of other components. In other cases, various crystals of more complex composition may be formed.

It is naturally important to take all this into consideration in studying reactions in crystalline mixtures.

No less important in this respect is the relationship between

- 31 -

the properties and structure of real crystals. As we know, while irreversibly disturbed crystalline systems possess reproducible properties in many respects, certain properties of irreversibly disturbed systems are functions of the disturbances and depend on the prior treatment of the specimen.

Many properties of crystals bear different relationships to disturbances in the regularity of their structure: some properties depend little or not at all on the preliminary treatment of the crystal, while others are essentially related to it.

On this basis, the properties of crystalline systems may be classified as follows:

1) structure-insensitive properties, e.g., refractive index, heat capacity, and melting point;

2) structure-semisensitive properties, e.g., the conductivity of ionic crystals, diffusion, and vibration damping;

3) structure-sensitive properties, e.g., tensile strength, plasticity, thermal conductivity, dielectric constant, magnetic susceptibility, magnetic permeability, and chemical activity.

The dependence of the properties of substances on their crystalline structure is widely exploited by contemporary technology not only to raise their chemical activities, but also to produce materials for various critical purposes (crystal phosphors, semiconductors, ferroelectrics, and piezoelectrics, and others) with prespecified properties. These materials are produced by careful regulation of defects in the crystal structure.

§ 4. POWDERED (GRANULAR) SOLIDS

Reactions between crystalline reagents usually take place with the reagents in fine-grained (powdered) mixtures.

Naturally, the nature and rates of such reactions, together with

the quality of the products obtained from them, depend essentially on the physical structure and properties of the powdered solids. From this standpoint, their study is of great interest.

A powdered solid usually consists of a large number of individual grains in contact with one another on a very minor fraction of their total surface. The imperfect contact between the grains is that property of powdered masses that is of greatest importance for the chemical engineering of solids. Also of great importance are the granulometric composition, bulk (loose) weight, angle of repose, porosity, areas of total and contact surfaces, friability, dispersibility, storability, hygroscopicity, thermal and electrical conductivity, chemical activity, and so forth. In using powdered solids, it is necessary to take these parameters into consideration.

Current information concerning some of these properties of powders and the qualitative laws governing their changes under the influence of various factors (and data concerning the influence of such properties on the processes of physicochemical transformation of powdered solids) are far from adequate. Not only have we failed to set off their investigation as an independent field of endeavor, as has been the case, for example, with colloid research, but we are frequently not systematic enough in studying them, proceeding without the necessary theoretical foundations and generalizations. As Bal'-shin [47] quite properly remarked, "At the present time, W. Ostwald's phrase 'Universe of circumvented quantities' might be applied with much greater justification to the group of bodies with imperfect contact between their particles (which includes powdered solids — P.B. and A.G.) than to the colloids."

This judgement, which was pronounced more than 10 years ago, is unfortunately still valid even today.

Powder metallurgy, which studies the structure of metallic powders and its changes when sintered metals are produced, devotes a certain amount of attention to the general properties of powdered solids. A rather respectable number of experimental studies have been devoted to study of the properties of metallic powders. Certain of their results can be extended to granular materials used in the technology of adhesives, ceramic products, refractories and high-strength structural materials, as well as in the production of fertilizers, catalysts, and various other types of products.

However, extension of the knowledge gained by powder metallurgy to handling processes for granulated materials in other branches of engineering can be of only limited significance, since it is not always done properly and is frequently inadequate.

Actually, the work of powder metallurgy is frequently limited for the most part to study of the changes in the grain contact surfaces in deformation and heat-treatment (sintering) operations, and to investigation of the structure and properties of the powdered metal as a function of the size of the contact surface.

In the meanwhile, a considerably more detailed physical characterization of powdered solids (and, in particular, a characterization of their total and active surfaces) is necessary for their study and application, which also require research into the diffusion, sorption, chemical and many other processes that take place in such solids. As we know, the treatment conditions and processes applied to free-flowing (granular) solids in powder metallurgy and in other branches of engineering differ sharply from one another in the overwhelming majority of cases: when reactions are being conducted in mixtures of crystalline solids, we deal with much more profound changes and a much wider complex of such changes (see Chapter 3) than in the

mechanical and heat-treatment to which metallic powders are subject.

The physicochemical characterizations and certain properties of the powdered masses used in powder metallurgy and in other branches of engineering (e.g., in adhesives production) are also dissimilar. In the latter case, the powdered masses are, in accordance with their intended use, distinguished by considerably greater nonuniformity in granulometric and chemical composition, and frequently represent mixtures of many components the properties of each of which varies in a different manner during the process of treatment. Naturally, on a change in the chemical and granulometric composition of a powdered solid as a result of processes unfolding in it, its general properties also change accordingly (and frequently quite considerably). This further distinguishes the treatment processes applied to powdered solids in the technology of silicates and in the chemical industry from the corresponding powder-metallurgical processes.

Each grain of a granulated or powdered material may consist of a large number of elementary particles of the same or different chemical composition, structure, and properties. The shape of the grains in granulated and powdered materials, which is determined by their mode of origin (by the method of preparation for artificially produced grains) may take widely different forms. On the basis of shape, the grains of various materials can be classified into two large basic groups:

1) approximately isometric or equiaxial grains (these include spherical and polyhedral grains) and 2) nonisometric or nonequiaxial grains, among which we may note filamentary or acicular grains and flat grains (laminar grains, tabular grains, and the like).

There also exist a large number of intermediate grain shapes (between groups I and II, between subgroups of the second group, and

so forth), that approach one of the enumerated groups to one degree of closeness or another.

If a powdered solid has nonisometric grains, this has an effect on the spatial distribution of the grains and results in anisotropy in the powders.

A grain possesses a minimum reserve of potential energy (which is determined by the product of the grain weight by the height of its center of gravity above the horizontal plane) when its smallest dimension is oriented parallel to the force of gravity.

The probability W_i that a nonisometric grain will land on a given face after a free fall may be regarded in first approximation as proportional to its area S and inversely proportional to its potential energy U_i:

$$W_i = \frac{100\,\frac{S_i}{U_i}}{\Sigma\,\frac{S}{U}}. \tag{4}$$

Using this as a point of departure, Berezhnoy [49] showed that the probability of free fall onto a lateral face of a grain having the dimensions $\underline{a}$ x $\underline{a}$ x $\underline{na}$ increases rapidly as $\underline{n}$ increases to 2 and has reached almost 89% at n = 2 (Fig. 8). If the grain has the form of a rectangular parallelepiped and the dimensions $\underline{a}$ x $2\underline{a}$ x $3\underline{a}$, the probabilities that it will fall onto the corresponding faces are 3, 19, and 78%.

As was correctly noted by Berezhnoy, the absence of free migration of the grains in a powder substantially reduces the differences between these probability values, but does not equalize them. As a result, elongated grains tend to arrange themselves parallel to the horizontal plane in a powder mass; this sometimes results in considerable differences in the properties of the mass in different directions [49, 50].
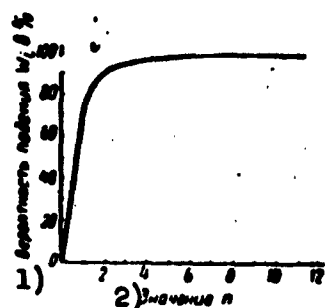
Fig. 8. Curve of probability of fall onto lateral face of grain having the dimensions a x a x na. 1) Probability W_1 of fall in %; 2) values of n.

Since the grain shape of a powdered material determines its properties to a considerable degree and may be strongly manifested in the properties of a product produced from it, it is important in many practical cases to be able to regulate the shape of the grains in the process of preparing powdered materials. Investigations recently carried out in this direction have made it possible to develop certain simple and reliable methods of grain-shape control for powdered materials. These include, for example, metastable crystallization from heavily supersaturated solutions, a process studied by Gzhimek [51].

The shape of the grain surfaces in a powdered material, the roughness and energy of which [surfaces], which also depend on the method and conditions used in producing the grains, may vary over extremely wide ranges, are of great practical importance. According to Khedval [52], the following are effective ways to regulate the surface activities of solids:

1) creation of defect lattices by modification transformations, oxidation and reduction processes, and the injection of foreign atoms into the lattices;

2) utilization of the magnetic state (ferromagnetic catalysts);

3) polarization changes in the state of the molecules;

4) electromagnetic and ultrasonic irradiation;

5) adsorption and solution of gases.

The grain sizes of powdered materials employed in technology, which depend on the conditions under which they were prepared and

influence their properties and the rate of processes that take place
in them, vary over a very wide range extending from tenths of a
micron to several millimeters. Certain granulated masses used to
effect reactions between solids in the metallurgical and chemical
industries contain grains with sizes ranging up to 1 cm and above.

Monodisperse and polydisperse powders are distinguished in ac-
cordance with whether the grains of a given powder mass are of the
same size or of different sizes. Normally, powdered materials of
natural and artificial origin are polydisperse until they are care-
fully classified into grain-size fractions. Their granulometric
composition is characterized by various methods [53], e.g., by
screen analysis, which has been described on numerous occasions in
the literature [see, for example, 54, 55].

The results of screen analysis enable us to judge the weight
percentage composed by each fraction of the material, and give a more
or less detailed representation of its granulometric composition;
this will be the more complete the narrower the range of grain sizes
within the limits of the individual fractions. Sometimes, for ex-
ample in the production of adhesives and refractory materials, the
fineness of a powdered material is characterized only by its content
of grains whose dimensions exceed a certain size. For example, it
may be stated that the residue on a No. 0085 screen is 10%, i.e.,
that 90% of the screened material has grain sizes below 0.085 mm
and 10% of it is larger than 0.085 mm. Such a characterization of
the grain composition of a material is frequently adequate for indus-
trial conditions. However, in that it indicates only the lower limit
of grain sizes "of the coarse fraction" and the upper limit of sizes
in the "fine" fraction (the principal fraction in the example cited
above), this characterization does not provide a conception of the

true granulometric composition of each of them nor, accordingly, of the material as a whole.

Strictly speaking, even the narrowest fraction of a powdered material contains grains of different sizes, i.e., it is not mono-disperse. The average grain size of a fraction may be computed from one of the known rules [53, 56].

If the ratio of the largest and smallest grain diameters which correspond to the width of the holes in "coarser" and "finer" screens, $d_b : d_m \leq 1.5$, the average grain diameter may be computed without any essential error as the arithmetical mean, geometrical mean, harmonic mean, Andresen mean, and so forth. Here, the number of "conventional" average-diameter grains computed by the Andresen method

$$d_{cp} = \sqrt[3]{\frac{2d_6^2 \, d_m^2}{d_6 + d_m}} \cdot \tag{5}$$

is found equal to the average number of grains in the fraction.

In the case of a mixture of grains having considerable size differences, i.e., when we are concerned with a broad fraction ($d_b : d_m > 1.5$), the value of d_{sr} may be computed by various methods.

At the present time, more than 50 different formulas have been proposed for calculation of average grain size in a mixture.

According to formulas of one group, the average-diameter value is computed taking the granulometric composition of the material to be averaged into account. When formulas of another group are used, the value of d_{sr} is found only from the size of the limiting diameters — those bounding the mixture being averaged — without taking the granulometric composition into account.

The most detailed critical characterization of all these formulas was given by Andreyev [53]. He showed that the values obtained by the various formulas for the average diameter of grains in the

2-60-μ fraction vary between 3.2 and 48 μ. It is clear in the light of this that arbitrary selection of a method for computing the average diameter (e.g., the most frequently encountered practice of computing it as the arithmetical mean value of the two extreme grain size in the fraction) may result in essential errors that increase as the range of grain sizes in the fraction is broadened.

As we know from mathematical statistics, different methods are used to calculate an average quantity in accordance with the property of a statistical collective that must be reflected in it. According to this, as Andreyev quite properly reasons, the average grain diameter should be computed to reflect some single, so-called determining parameter of an ensemble of grains. This means that the formula selected for the averaging should be one whose application leaves the determining parameter of interest to us unchanged.

Thus, if the surface area of all grains is determining, the average diameter should be computed by the formula

$$d_{cp} = \sqrt{\frac{\Sigma n d^2}{\Sigma n}}. \tag{5a}$$

i.e., as the root-mean-square diameter weighted over the number of grains.

If the determining parameter is the volume of all grains, the average diameter is computed as the root-mean-cube diameter weighted over the number of grains:

$$d_{cp} = \sqrt[3]{\frac{\Sigma n d^3}{\Sigma n}}. \tag{5b}$$

If the specific surface area of the grains, i.e., the ratio of their surface to their volume (or to their weight) is determining, then

$$d_{cp} = \frac{\Sigma n d^3}{\Sigma n d^2} \tag{5c}$$

or, in terms of weight,
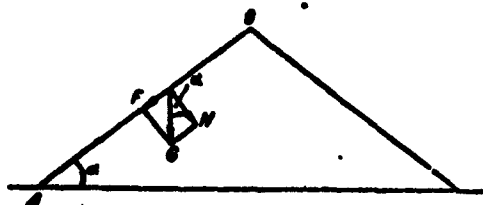
Fig. 9. Angle of repose of powdered material.

$$d_{cp} = \frac{\Sigma G}{\Sigma \dfrac{G}{d}} \qquad (5d)$$

and so forth.

In these formulas, $\underline{n}$ is the number of grains in the individual narrow fractions of the mixture, $\underline{d}$ is the variable diameter of grains of different sizes in the mixture to be averaged, d_{sr} is the constant average diameter of grains having the same size, and G is the weight of the individual narrow fractions.

Within the practical grain-size ranges indicated above, the number of grains in a unit volume of powdered material may be extremely large (1 cm^3 may contain millions and even billions of grains). Naturally, many physical properties of the powder are determined by the mutual spatial arrangement of its grains and are statistical in nature. Such properties include the bulk characterization of the powder: its angle of repose, its porosity, bulk weight, and certain other quantities.

If the grain weight G (Fig. 9) is decomposed into two components, one normal to the plane AB:

$$N = G\cos\alpha$$

and one tangent to it,

$$F = G\sin\alpha,$$

then

$$F = N\,\mathrm{tg}\,\alpha. \qquad (6)$$

A powder grain will be at rest when the force F is offset by the frictional force P. The latter is porportional to the normal pressure:

$$P = \mu N,$$

where μ is the coefficient of friction. It follows from this that

$\mu = \alpha$, i.e., that the angle of repose α is equal to the coefficient of friction.

The value of α, which generally depends on the size and shape of the grains in the material, the nature (roughness) of the material's surface, its moisture content, and certain other parameters, lies in the range from 35 to 50° for the majority of air-dry loose-pouring solids. As we know, a certain fraction of the volume of a granular material is frequently occupied by pores inside its grains; these compose the so-called intragranular porosity; as a result of surface porosity and the imperfect fit between the grains of the powder, a considerable fraction of its volume belongs to the free space between the surfaces of the granules.

The part taken by the pores depends on their type (intraparticle, interparticle), sizes (which may be macroscopic, microscopic, or submicroscopic) and their type. Pores are subdivided into open types (communicating or capillary pores) and closed types (isolated pores). Intraparticle pores may be either open or isolated; interparticle pores in unpressed powders always communicate with one another and with the surface of the granulated material. The total porosity (or free surface) of a free-pouring granular material, expressed as the relative volume of the powder occupied by the interparticle and intraparticle pores, usually lies between 50 and 80%, sometimes reaching 95-98%. It value naturally determines the specific volume and loose weight of the powder. For a given specific-weight value of the powder material, its loose weight is a complex function of its granulometric composition (absolute value and range of grain sizes, ratio between amounts of individual fractions), the nature of the grain surface, the pressure exerted by overlying layers, moisture content, and impurity content.

- 42 -

Variation of certain of these parameters may increase or reduce the porosity and loose-weight value of the powder by 50-80% or more. Consequently, the frequently encountered indications of the bulk (loose) weight of granular materials without an accompanying indication of their granulometric composition, moisture content, or other conditions are always inadequately specific.

In the simplest case, in which the grains are spherical and all have the same diameter, each of them is in contact with its neighboring grains at 6, 8, or 12 points, in accordance with the manner of their distribution in space (cubic, rhombohedral, hexagonal); this corresponds to a free-space volume (porosity) between the grains ranging from 47.64 to 25.95%. These data, which characterize the geometrically regular spatial arrangements of absolutely smooth incompressible dry spheres in contact at specific mathematical points, naturally have little correspondence to the properties and behavior of real loose-poured crystalline masses. In actuality, due to the irregular shape and surface roughness of the particles of fine-grained substances, and due to the presence of frictional and adhesive forces between them, it is not only impossible to obtain ideally close packing of these particles (corresponding to a free-space value $V_{sv} = 25.95\%$), but even to count on free, geometrically regular arrangements of the particles (corresponding to $V_{sv} = 47.64\%$). The grains composing real masses have different distances from one another: some neighboring grains are in relatively close contact with one another, while the distances between other neighboring grains are very large, and so forth. The shape irregularities and roughness of the grains in real masses have as a consequence that the distance between different segments of the surface of any given grain and the surfaces of the grains surrounding it varies over an extremely wide range.

- 43 -

However, in considering any given fine-grained mass, we may speak of a certain average value of the distance between the surfaces of its grains — one that will be characteristic for this mass. This quantity, which is an extremely important one for analysis of reaction mechanisms in mixtures of solids, may be determined easily as follows.

If a unit of the total volume of a loose-poured mass consists of $\underline{n}$ spherical grains having a average diameter d_z and, accordingly, $\underline{n}$ airspaces with an average diameter d_p which, taken together, compose a free space of volume V_{sv} (in fractions of unity), then the volume of the particles themselves will be

$$1 - V_{co} = n\frac{\pi d_s^3}{6} \tag{7}$$

and the airspace volume will be

$$V_{co} = n\frac{\pi d_s^3}{6}. \tag{8}$$

Hence the average diameter d_p of a single airspace or, in other words, the average distance $\underline{l}$ between grains will be

$$l = d_n = d_s\left(\frac{V_{co}}{1-V_{co}}\right)^{\frac{1}{3}}. \tag{9}$$

If, further, γ_v is the average apparent particle (grain) specific gravity, the volume of a unit weight of granular material, which will be composed of the total particle volume $1/\gamma_v$ and the volume of the interparticle pores, will be

$$V_{нася} = \frac{\frac{1}{\gamma_s}}{1 - V_{co}} \tag{10}$$

and since the loose weight of the material

$$\gamma_n = 1 : \frac{\frac{1}{\gamma_s}}{1-V_{ca}} = (1 - V_{co})\gamma_s, \tag{11}$$

then

$$V_{co} = 1 - \frac{\gamma_n}{\gamma_s}. \tag{12}$$

Substituting the value of V_{sv} from Formula (12) in Equation (9), we have

$$l = d_s \left(\frac{\gamma_0 - \gamma_s}{\gamma_s} \right)^{\frac{1}{3}}.$$

(13)

Thus, knowing the loose weight of the fine-grained mass, the average size of the grains composing it, and the apparent specific gravity of the latter, we may draw inferences concerning the average distance between the surfaces of contiguous grains in this mass.

Equation (13), which applies for spherical grains, reflects, with an accuracy sufficient for practical purposes, the average distance between the surfaces of contiguous grains in fine-grained masses in which the grains take almost any shape.

Determination of the value of $\underline{l}$ in real masses may be complicated somewhat simply by the difference between the values of the true and apparent densities of the material of which the particles are composed and by the error in determining the latter. However, the total volume of the intraparticle pores, which is responsible for this difference, is shown by data from investigation of crystalline inorganic substances to lie in most cases between 0.5 and 15% of the grain volume and, accordingly, not to exceed 7% of the loose volume of the powder.* If we take into account here that the volume of the interparticle pores generally composes no less than 50% of the loose volume of a granular mass (see, for example, the data of Table 8), then it is easy to establish that the value of the true specific gravity of the particle material may be substituted into Eq. (13) instead of γ_v to ascertain the order of magnitude characteristic of the granular mass.

To characterize the properties of fine-grained crystalline materials in connection with their reactions in mixtures, it is

interesting to give an experiment-based indication of the order of magnitude of the average distance between the surfaces of contiguous grains in the real masses. With this objective, Ginstling [57] at one time investigated a large number of fine-grained crystalline materials.

All of these substances were carefully coarseness-classified for determination of their loose-poured weight. Then 2, 3, and 4 narrow fractions were extracted from each material. The average grain size within the limits of each narrow fraction was calculated by Eq. (5).

TABLE 7

Grains Sizes in Fractions of Fine-Grained Materials

1) Пределы размеров зерен фракции в мм	2) Средний размер зерна в мм	1) Пределы размеров зерен фракции в мм	2) Средний размер зерна в мм
0,35—0,27	0,306	0,20 —0,135	0,163
0,35—0,25	0,294	0,135—0,120	0,177
0,27—0,25	0,259	0,102—0,088	0,095
0,25—0,20	0,223	0,088—0,060	0,072

1) Range of grain sizes in fraction, mm; 2) average grain size, mm.

Table 7 presents data characterizing the basic fractions extracted from the fine-grained materials.

To provide a basis of judging γ_n, V_{sv}, and $\underline{l}$ as functions of particle size in the fine-grained mass, the loose-poured weights of "coarse" and "fine" fractions and a mixture consisting of equal volumes of these were determined for each substance. Table 8 presents some of the results of determination* run on various inorganic substances of commercial importance. These experimental data indicate that

1) the spatial arrangement of grains in real fine-granular masses apparently differs essentially from any "theoretical" arrangement of smooth spherical particles;

2) as a rule, the porosity of such masses composes 50 to 80%,

- 46 -

TABLE 8

Characterization of Inorganic Crystalline Fine-Grained Substances

1) Наименование вещества	2) Средний размер зерна в мм	3) Удельный вес вещества $\gamma_в$	4) Насыпной вес зернистой массы $\gamma_н$	5) Пористость массы $V_{св}$ в %	6) Среднее расстояние между поверхностями соседних зерен l в мм
1	2	3	4	5	6
Al_2O_3	0,095 0,072 0,079	3,99	0,998 1 1,013	75,4 75,3 75,1	0,14 0,1 0,11
$Al(OH)_3$	0,127 0,072 0,082	2,26	1,21 1,11 1,18	46,5 50,9 49,8	0,12 0,07 0,08
$Al_2(SO_4)_3$	0,163 0,095 0,107	2,71	0,532 0,518 0,55	80,4 80,9 79,8	0,26 0,15 0,17
AlF_3	0,127 0,095 0,107	2,5	0,671 0,648 0,675	73,2 74,1 73	0,18 0,13 0,15
$BaSO_4$	0,259 0,072 0,076	4,46	1,2 1,05 1,20	73,1 76,4 73,1	0,36 0,1 0,11
Fe_2O_3	0,163 0,072 0,078	5,1	1,04 0,99 1,12	79,7 80,6 78	0,26 0,12 0,12
KNO_3	0,306 0,095 0,104	2,11	0,973 0,72 0,827	53,7 65,8 60,7	0,32 0,12 0,12
$K_2Cr_2O_7$	0,294 0,095 0,106	2,7	1,26 0,94 1,21	53,3 65,2 55,2	0,31 0,12 0,12
$CaSO_4 \cdot 2H_2O$	0,306 0,095 0,104	2,2	0,89 0,69 0,85	59,6 68,7 61,4	0,35 0,12 0,12
$CaCO_3$	0,163 0,095 0,107	2,71	0,506 0,507 0,515	81,3 81,3 81	0,27 0,16 0,17
CaF_2	0,163 0,095 0,107	3,1	1,15 1,11 1,16	63 64,2 62,6	0,19 0,11 0,13
SiO_2	0,306 0,095 0,209	2,65	1,42 1,4 1,48	46,5 47,2 44,2	0,29 0,09 0,18
MgO	0,306 0,127 0,195	3,45	0,204 0,188 0,23	94,09 94,56 93,86	0,77 0,33 0,47
$MgSO_4 \cdot 7H_2O$	0,306 0,095 0,163	1,68	0,725 0,477 0,677	56,9 71,7 59,7	0,33 0,13 0,19
$CuSO_4 \cdot 5H_2O$	0,306 0,095 0,163	2,29	1,04 0,715 1,02	54,6 58,8 55,5	0,33 0,12 0,18
$Na_2SO_4 \cdot 10H_2O$	0,163 0,095 0,107	1,46	0,7 0,66 0,72	51,7 55 50,4	0,17 0,1 0,11
NaF	0,095 0,072 0,077	2,73	0,952 0,952 1	65,2 65,2 63,4	0,12 0,09 0,09

TABLE 8 (Cont'd.)

NaCl	0.163 0.095 0.107	2.16	0.927 0.843 0.892	57.1 61 58.8	0.18 0.11 0.12
(ClF)Ca₃ (PO₄)₃ (апатит) [7]	0.163 0.095 0.107	3.2	1.56 1.54 1.59	51.1 52 50.4	0.17 0.1 0.11
mAl₂O₃·nH₂O·nFe₂O₃·qSiO₂	0.239 0.095 0.147	2.58	1.1 0.98 1.04	56.9 61.6 59.2	0.29 0.11 0.17

Note: In the table, γ_v represents the true specific
gravity of the particle material, while V_{sv} repre-
sents the total (intraparticle and interparticle)
porosity of the mass. The third line for each sub-
stance in columns 2, 4, 5, and 6 characterizes a
mixture of equal volumes of the two fractions indi-
cated in the first two lines of the column.

1) Substance; 2) average grain size in mm; 3) specific
weight of substance, γ_v; 4) loose-poured weight of
granular mass, γ_n; 5) porosity of mass, V_{sv} in %;
6) average distance between surfaces of contiguous
grains, $\underline{l}$ in mm; 7) apatite.

as against a porosity of 26-48% for a mass composed of smooth spheres;

3) the values of the average distance $\underline{l}$ between the surfaces

of contiguous grains in the real mass and the average diameter d_{sr}

of the grains are of the same order; $\underline{l}$ comes to ~120 to 150% of d_{sr};

4) when the grains composing the mass are of the same size,

the porosity of the mass will be higher than when they have different

sizes;

5) if the mass consists of particles (grains) of approximately

the same size, the porosity of this mass and, accordingly, the aver-

age relative distance between the surfaces of its grains will in-

crease as the particle size diminishes.

These data are in full agreement with theory. Naturally, the

loose application of the rough surfaces to one another results in the

appearance of considerable free space between them. A decrease in the particle size in the mass, which results in an increase in the surface area of these particles per unit weight, gives rise to a corresponding increase in the internal friction and cohesiveness ("strength") of the mass. The latter is nicely confirmed by the data presented in Table 9 on the value of the angle of repose for certain fine-grained materials. A result of this increase in the "strength" of the mass is an increase in its porosity. The lower porosity of a polydisperse mass as compared with a monodisperse mass of the same substance is the result of filling of the spaces between coarser grains by finer grains, etc.

TABLE 9

Angle of Repose of Loose-Poured Masses for Various Grain Sizes

1) Наименование вещества	2) Размер зерен в мм	3) Угол естественного откоса
BaSO₄	0,25 —0,08 0,088—0,08	41°08' 45°
KNO₃	0 35 —0,27 0,102—0,088	38°40' 45°
NaCl	0,2 —0,135 0,102—0,088	39°42' 41°08'
AlNH₄(SO₄)₂·12H₂O	0,35 —0,27 0,2 —0,135	36°53' 45°

1) Substance; 2) grain size in mm; 3) angle of repose.

In view of the great practical importance of porosity, its numerical value is frequently regulated by selecting the granulo-metric and chemical composition of the initial material and the conditions used in sintering it.

It has been established by the investigations of Berezhnoy [49], for example, that minimal porosity can be attained in the product (refractory material) by roasting a mixture of two fractions of the initial powder having an average-grain-size ratio (coarse to fine fraction) of 30 and containing 60 to 70% of the former and 40 to 30%

- 49 -

of the latter.

The total and contact grain-surface areas of a granular material are among its most important parameters. The first of these areas is determined by the grain sizes and the degree of surface roughness.

On dividing a cube having a side length $\underline{a}$ and a surface area $6a^2$ into cubes having a side a/n, we obtain n^3 cubes having a total surface area of

$$n^3 \frac{6a^2}{n^3} = 6na^2.$$

Thus, the specific surface area (surface of a unit weight) of a granular mass is inversely proportional to its grain size. Below we present values of the total surface area of a body corresponding to different degrees of fractionation.

1) Длина ребра кубика в см		1	$1 \cdot 10^{-1}$	$1 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-7}$
2) Общая площадь поверхности кубиков в см²	6		$6 \cdot 10$	$6 \cdot 10^2$	$6 \cdot 10^3$	$6 \cdot 10^4$	$6 \cdot 10^5$	$6 \cdot 10^6$	$6 \cdot 10^7$

1) Length of cube side in cm; 2) total surface area of smaller cubes, cm^2.

The distribution of the total grain surface area of a polydisperse powder among its various fractions is worthy of attention. Practical experience indicates that even with a relatively small weight content of the finer fractions in a powder mixture, they usually account for a highly significant fraction of the total grain-surface area. This is one of the principal causes for the differing rates of physicochemical transformations observed for the various fractions.

Due to the fact that in a granular mass, the surfaces of contiguous grains are, on the average, separated from one another by
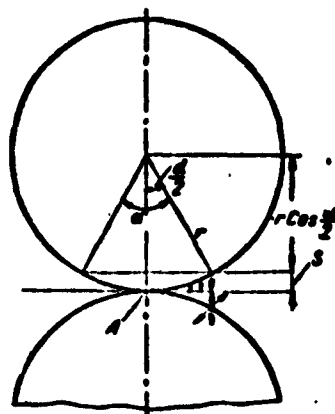
Fig. 10. Diagram of contact be-
tween two spherical grains.

a distance that exceeds their dia-
meter by a factor of 1.2 to 1.5, the
contact area differs considerably
from the total grain-surface area.

It would be of interest to
ascertain the possible relationships
between the contact and total surface
areas of a loose-poured mass.

We shall regard surfaces as
being in contact if the distance be-
tween them does not exceed the effective radius of the molecular
forces. As we know, the size of this radius is reckoned in Angstroms,
i.e., is of the order of 10^{-8} cm. Depending on the conditions under
which the various solid-phase processes are effected in the tech-
nology of silicates and alumina and in electrothermal and other proc-
esses, the average grain size of the initial reagents may be assumed
to lie between 1 and 10^{-3} cm.

Let us now return to smooth, dry spherical particles (grains)
of uniform diameter. Let two such particles of radius r be in con-
tact at a certain point A (Fig. 10). Let S denote the effective mole-
cular-force radius and α the central (solid) angle subtended by that
part of the spherical surface of any of the grains that comes into
the sphere of influence of the molecular forces of another grain. The
cosine of half this angle may be determined from the equality

$$S = r\left(1 - \cos\frac{\alpha}{2}\right). \tag{14}$$

For $S = 10^{-8}$ cm and $r = 10^{-1}$ to 10^{-3} cm, we find from Eq. (14)
that α may assume values from a few (1-2) seconds to several minutes;
this corresponds to a theoretically possible contact-surface area
between particles ranging from 10^{-7} to 10^{-4} of the total surface area

- 51 -

of these particles.

The results of a number of investigations [47, 58, 59] indicate that in real masses, the area of the contact surface between their grains is reckoned in millionths and even ten-millionths of the total grain-surface area.

If, regarding the grains as spherical, we assume that the free space between them is equal to 50% of the total volume of the loose-poured mass that they compose, and that the contact area between them is, in accordance with experimental data, reckoned in quantities of the order of 10^{-4}% of their total surface area, it will be easy to obtain approximate values for the contact area between the grains in powders and granulated masses of various grain sizes (Table 10).

TABLE 10

Typical Values of Contact Surface Area Between Particles of Fine-Granular Mass.*

1) Диаметр зерна в см	2) Объем зерна в см³	3) Поверхность зерна в см²	4) Число зерен в 1 см³ массы	5) Поверхность зерен в 1 см³ массы в см²	6) Примерная поверхность контакта между зернами на 1 см³ массы в см²
1	$5,23 \cdot 10^{-1}$	3,14	$9,57 \cdot 10^{-1}$	3	$3 \cdot 10^{-3}$
$5 \cdot 10^{-1}$	$6,54 \cdot 10^{-2}$	$7,84 \cdot 10^{-1}$	7,64	6	$6 \cdot 10^{-4}$
$1 \cdot 10^{-1}$	$5,23 \cdot 10^{-4}$	$3,14 \cdot 10^{-2}$	$9,57 \cdot 10^{2}$	$3 \cdot 10$	$3 \cdot 10^{-4}$
$5 \cdot 10^{-3}$	$6,54 \cdot 10^{-5}$	$7,84 \cdot 10^{-3}$	$7,64 \cdot 10^{3}$	$6 \cdot 10$	$6 \cdot 10^{-4}$
$1 \cdot 10^{-2}$	$5,23 \cdot 10^{-7}$	$3,14 \cdot 10^{-4}$	$9,57 \cdot 10^{5}$	$3 \cdot 10^{2}$	$3 \cdot 10^{-3}$
$5 \cdot 10^{-3}$	$6,54 \cdot 10^{-8}$	$7,84 \cdot 10^{-5}$	$7,64 \cdot 10^{6}$	$6 \cdot 10^{2}$	$6 \cdot 10^{-4}$

*Computed assuming that the grains are spherical and $V_{sv} = 50$%.

1) Grain diameter in cm; 2) grain volume in cm^3; 3) grain surface area in cm^2; 4) number of grains in 1 cm^3 of mass;
5) surface area of grains in 1 cm^3 of mass, in cm^2;
6) approximate contact-surface area between grains per 1 cm^3 of mass, in cm^2.

Obviously, the rough surfaces of the particles in real masses will be many times their apparent surface area, and this will apply with greater force to the surface area of spheres of the same size. Values exceeding the apparent surface area as computed on the basis

of microscopic measurements of grain size [60, 61] by hundreds and thousands of times have been obtained by determining the true surface area of powdered masses by the dye-adsorption method. However, the same roughness interferes with contact between particles, tending to hold them apart (Fig. 11a, b, c, d). Consequently, we may, without incurring any significant error, assume the order of magnitude of the contact surface between particles of fine-grained masses to be identical to those indicated in Table 10.

Shaken and pressed granular solids, which are frequently used in research and industrial practice, differ considerably as regards their parameters from free-poured powders. The porosity of the shaken powders usually runs to only 35 to 70 (sometimes 80) % as a result of the closer approximation of the grains.

In the majority of cases, the total and contact areas of the grains remain essentially the same after the shaking process.

The following basic changes take place in a real granular mass when it is compressed (pressformed) with sufficient force:

a) the average distance between the surfaces of contiguous grains is reduced;

b) the shape and area of the grain surfaces change;

c) the contact-surface area between the grains changes.

Theoretically, compression of such a mass may also result in a certain reduction in the intraparticle porosity and in a resulting increase in the apparent density of the grains. However, the compressibility of solids is, as we know, negligible. Deformation of powder masses naturally takes place at the expense of the first and second of the phenomena enumerated above, to the extent that they can take place at all. Under practical conditions, therefore, the increase in the apparent density of the actual grains as the pressure on the
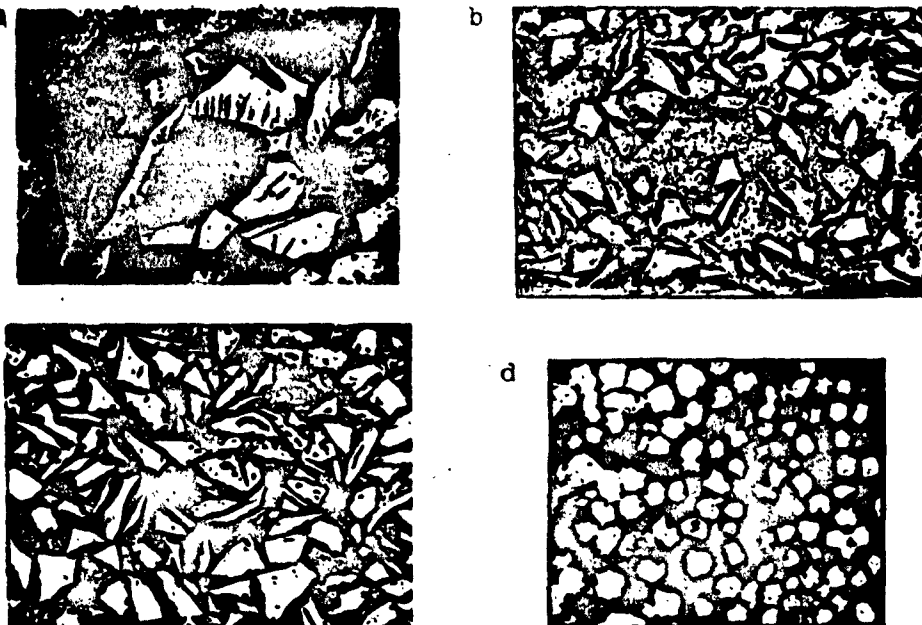
Fig. 11. Arrangement of grains in powdered masses.
a) Anthracite powder (44x); b) anthracite powder
(86x); c) close-shaken anthracite powder (86x);
d) metallic-copper powder produced by reduction of
$CuSO_4$ (250x).

mixture rises can be disregarded.

As regards the distance between the surfaces of the grains, the reduction that it suffers in the compression process may be quite considerable. Given sufficiently large compression pressure supplied to a powdered material, its porosity can be reduced practically to zero. The grain-surface contact area also undergoes a considerable change on compression. It has been shown experimentally [58, 59] that the contact-surface area (more precisely, the area S of the projection of the contacting sections onto a plane normal to the direction of the pressure) is proportional to the compressing pressure.

If a certain pressure acts on two bodies in contact with one another at supporting contact projections and compresses them, the increase in their contact-surface area begins when the specific pressure exceeds the critical stress σ_k of the material, at which it

- 54 -

begins to deform plastically. For a constant value of the pressure, this increase in the area S continues until the specific pressure is reduced to the value σ_k.

An increase in contact area may take place either because of an increase in the area of the existing contact zones as a result of plastic or brittle deformation of the material, or as a result of the appearance of new contact points. The true picture of the increase in contact area may be more or less complex, depending on the relative spatial arrangements of the individual grains, the relationship between their strength values, the presence and distribution of superficial impurities, and certain other factors. An increase in contact area on compression may also take place as a result of the appearance of depressions on the grain surfaces under pressure from projections on other grains, in accordance with the description given by R. Barta [62], and as a result of crushing of high spots, as is most frequently assumed in powder metallurgy.

The significance of each of these phenomena may vary, depending on the conditions of the process.

When a granular material is heated, the total and contact areas of its grains may undergo essential changes. The nature and qualitative laws of these changes will be associated to a considerable degree with the phenomena of sintering and recrystallization to be considered below (Chapter 2, § 2). Here we note only that even simple thermal expansion of the grains of a free-poured powder on heating may result in an irreversible filling of its pores, i.e., in reduced porosity and increased contact area (the reverse effects are also possible on heating of pressformed granular masses [47, 63, 64]).

The natural and technical conditions prevailing in formation of crystalline bodies, and crystalline powdered material in particular,

- 55 -

together with the high specific porosity of the latter, are respon-
sible for the presence of foreign impurities in them. Strictly
speaking, one quantity or another of impurities in crystals is
practically inevitable in all cases when they are produced from
either the liquid or gaseous phase by crystallization, or from the
solid phase by reacting it chemically with other substances.

It has been established that even when the conditions for
separating a solid phase from a solution or melt are most carefully
observed with the objective of obtaining "pure" crystals, they still
contain a certain quantity of impurities [46, 63].

Fig. 12. Adsorption isotherm
in case of capillary condensa-
tion. 1) Adsorption; 2) pres-
sure; 3) P_{nas}.

It is also known that crystals
produced by oxidation, reduction, or
exchange decomposition of other cry-
stals always incorporate a certain
quantity of the initial substances
[46, 63].

A considerable quantity of im-
purities is concentrated at the sur-
faces of the grains in crystalline

disperse masses as a result of adsorption. According to Tshebyatov-
skiy [64], 1 g of powder is capable of adsorbing several cubic centi-
meters of gas. As we know, the process of gas adsorption by a solid
results in a reduction of the solid's surface tension (as a result
of saturation of some of the uncompensated forces at its surface) and
hence in a reduction of the system's free energy, and is spontaneous.

As a result of the large number of capillaries and pores in
many crystalline solids, the so-called capillary-condensation phenome-
non may exert considerable influence on the process in which they ad-
sorb liquids. When the walls of narrow capillaries are well wetted by

- 56 -

a liquid, the liquid surface in such capillaries takes the form of a concave meniscus. The saturation vapor pressure above such a surface, as determined by the Thomson equation, is lower than the saturated-vapor pressure above a flat surface of the same substance.

As a result, a vapor that would be unsaturated with respect to a flat surface may prove to be saturated or even supersaturated if it is above the surface of a fluid inside the capillaries of a solid. This is what gives rise to capillary condensation. Its presence is characterized by a specific bend in the adsorption isotherm as it approaches the saturated-vapor pressure (Fig. 12). The position of this bend depends on the nature of the pores in the adsorbent.

Finally, a considerable quantity of impurities (contamination) sometimes results from mechanical or chemical attrition of the apparatus in which the grinding, roasting, and other processes are applied to the solid phases.

The impurity content in the technical raw materials and products used in industry are virtually always quite considerable. However, even a "negligible" impurity content in a crystalline solid, as may sometimes arise in research practice, may exert considerable influence on the strength of the solid's lattice [8, 33, 46, 63], on its surface energy [29], and on its properties [33, 46, 60, 65]. Consequently, it is not admissible to disregard even a small impurity content in a disperse crystalline body in analysis of the processes taking place in it.

We distinguish intraparticle and interparticle impurities. The latter include, for example, surface impurities (on the grain surfaces of a disperse solid), extremely thin layers of which (of the order of microns and fractions thereof) may influence processes of mechanical deformation, sintering, recrystallization, and chemical

transformation of crystalline solids.

[Footnotes]

18   *G. Mi [3] proposed taking the increased effect of the
repulsive forces at elevated temperatures into account
by introducing a third term in Eq. (1) (with the same
sign as the second):

$$C(T)/r^{n_3},$$

where $C(T)$ is a certain function of temperature and
symbatic to it, and n_3 is a constant that will obviously
depend on the nature of the lattice and the properties
of the solid.

18   **According to contemporary conceptions [10, 14-18], the
lattice bonding energy reduces to the energy of the valence
electrons within the ion field.

19   *In 1955, Kapustinskiy and Yatsimirskiy [21] took into
consideration the dependence of the coefficient ρ on the
distance between ions:

$$\rho = 0.345 - 0.00435 \, (r_1 + r_2)^2,$$

thereby further refining the expression for the lattice
energy of ionic crystals

$$U = 287.\frac{\dots \Sigma n}{r_1 + r_2}\left[1 - \frac{0.345 - 0.00435\,(r_1 + r_2)^2}{r_1 + r_2}\right]\text{kcal/mole.} \qquad (3a)$$

24   *There is as yet no dependable method for measuring the
surface energy of solids.

26   *We use the term "imperfect" for a crystal that has the
stoichiometric composition but structural defects [33].

45   *The only exceptions to this are sorbents, refractories,
heat-insulating, and other materials whose increased
porosity is created artificially.

46   *The properties of the overwhelming majority of substances
tested but not included in the table are analogous to the
properties of the compounds listed in it.

[List of Transliterated Symbols]

24   жидк = zhidk = zhidkost' = liquid
39   б = b = bol'shoy = large
39   м = m = malyy = small
39   ср = sr = sredniy = average
41   tg = tan

Chapter 2

BEHAVIOR OF SOLIDS ON HEATING

§ 1. THERMAL MOTION OF PARTICLES IN SOLID. DIFFUSION IN SOLIDS

How do crystalline substances behave on heating?

Many of the specific properties of the course of reactions in solid mixtures are naturally related to the answer to this question, which is a relatively simple one only at first glance.

It was believed until comparatively recently that the thermal agitation of particles in a solid reduces to oscillations of the atoms about their equilibrium positions, which are governed by the structure of the crystal lattice. It was known that the amplitude and frequency of these oscillations depend on temperature, but it was assumed that at any temperature up to the melting point of a crystalline solid, each of its particles was "tethered" to its own definite (nodal) point in the lattice. This conception, even when it had been further corrected for thermal expansion of the crystals, was not in agreement with the possibility of diffusion, solution (formation of solid solutions), and mutual-diffusion processes in solids.

According to Frenkel', these irreversible displacements reduce to dislodgement of the atoms from their initial equilibrium positions and transition to new equilibrium positions at lattice points or in lattice interstices that had previously been vacant. Such transitions are naturally accompanied by the appearance of defects in the crystal structure — the "holes" and dislocated atoms noted earlier. As shown

by Frenkel', the appearance and migration of holes is always possible and, more than that, inevitable; on the other hand, the implantation of atoms in the intervals between lattice points can be of essential importance only when there is a relatively large ratio between the size of the interstice and the radius of the dislocated atom [43].

In principle, it is quite possible for particles of a solid to migrate successively between lattice points (from an occupied point to a nearby vacant point), between interstices (from one to another adjacent interstice), and even between points and interstices (from a point into a neighboring interstice and vice versa). The result of this type of progressive elementary migration is diffusion of solids, which will be dealt with in detail below, and the formation of solid solutions, which is associated with it.

In the formulation of Kurnakov [66], crystalline phases in which the proportions between the components may vary without disturbance of homogeneity are known as solid solutions. It is customary to classify these crystalline phases into three categories or three types in accordance with their structure: substitutional solid solutions, interstitial solid solutions, and subtraction solid solutions.

In substitutional solid solutions that have formed on the basis of a chemical element, the atoms of the dissolved substance replace atoms of the solvent in the crystal lattice, becoming distributed statistically among them in the process (Fig. 13a). When a substitutional solid solution forms between chemical compounds of the types AB and AC, for example, NaCl and KCl, the atoms (or ions) of the components are arrayed in accordance with diagram b (see Fig. 13). In complex solid solutions of the same type — composition A, B, C, D — the atoms or ions are arranged in accordance with diagram c, and in those of composition A, AB (in solutions of a component A in a chemi-

- 60 -

cal compound AB), they are distributed in accordance with diagram d.

In interstitial solid solutions, the atoms of the dissolved substance are located in the interatomic interstices of the solvent crystal lattice. Solutions of this type are formed when nonmetals with small atomic radii are dissolved in certain metals. The interstitial solid solutions include, for example, austenite – a solution of carbon in γ-iron (Fig. 14). A distinctive structural property of interstitial solutions is the strong bonding between the interstitial atoms and the solvent atoms; this results in solutions of this type having high hardness and high melting points. Examples are the carbides of tungsten, molybdenum, titanium, vanadium, and iron and iron and titanium nitrides, which are important factors in contemporary metallurgy.

In subtraction solid solutions (also known as defect-lattice solutions), the atoms of one of the components normally occupy all normal positions, while certain positions of the second-component atoms remain vacant (Fig. 15). Solutions of this type are formed only on the basis of chemical compounds.

Subtractional solid solutions are known in which certain points belonging to different components of the solution are vacant. These include, for example, certain oxides of titanium, in which points "intended" for ions of both the oxygen and the metal are found vacant [67].

Due to the difference between the atomic radii of the solvent and the solute element, the crystal lattice of a substitutional solid solution is usually somewhat distorted (Fig. 16). Distortions of much greater severity arise on implantation of atoms of the solute substance in the interatomic interstices of the solvent, and on formation of vacancies in the crystal lattice, i.e., in formation

- 61 -
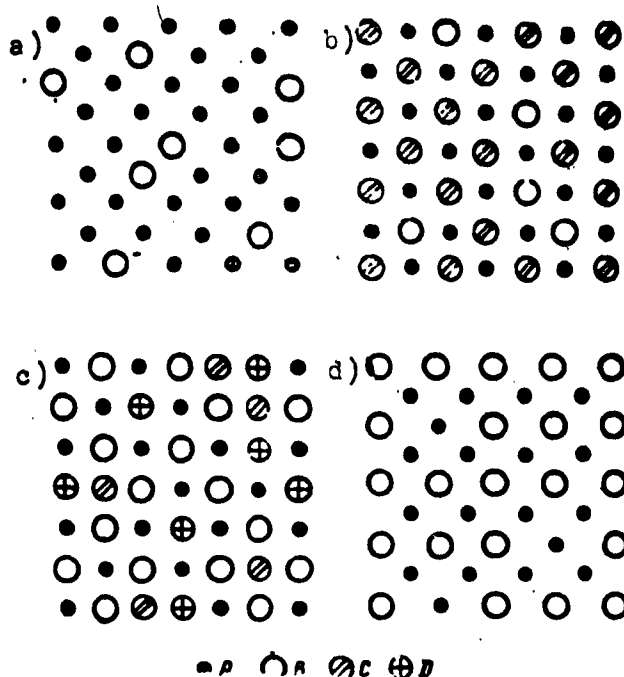
Fig. 13. Substitutional solid solutions. a) Between elements A and B; b) between the chemical compounds AB and AC; c) between the elements A, B, C, D; d) between elements A and compound AB.
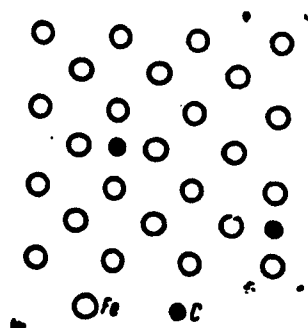
Fig. 14. Interstitial solid solution. (100) plane of austenite crystal.
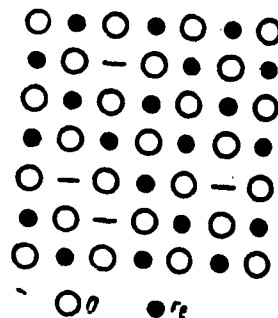
Fig. 15. Subtractional solid solution (wuestite).

of interstitial and subtractional solid solutions. The presence of such distortions is confirmed by the results of numerous experimental studies [67-72 and others].

It is obviously important to know the composition and structure of the solid solutions that arise in the course of a reaction

- 62 -
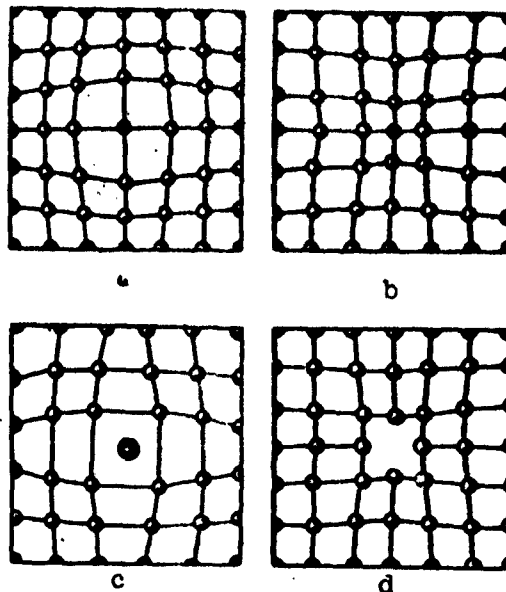
Fig. 16. Distortion of crystal lattice on forma-
tion of solid solutions. a, b) Substitutional;
c) interstitial; d) subtractional.

to draw inferences concerning the chemical activity of a given mix-
ture of crystalline reagents and to understand the nature of the
diffusion that accompanies chemical reaction in such a mixture.

The limited information available in this field represents a
serious hindrance to further study of reactions between solids.

According to Wegard's rule [73], the lattice parameter of a
solid solution is a linear function of its composition, i.e., it
varies linearly with changes in molecular concentration. In actuality,
this rule is seldom justified; in the majority of cases, we observe
deviations having only the positive sign (the lattice parameter of
a solid solution exceeds the value corresponding to the linear law)
or only the negative sign. Deviations of the second kind are en-
countered more frequently.

As shown by Pines [74], Wegard's rule may be exactly valid only
in cases of

   a) incompressible atoms, when the compressibility coefficients

of the solute and solvent atoms are equal to zero, $\kappa_1 = \kappa_2 = 0$ and

b) "elastic" atoms, in which case these compressibility coef-ficients are equal: $\kappa_1 = \kappa_2$.

In the general case with $\kappa_1 \neq \kappa_2$, deviations from linearity must take place, with the sign of the deviation determined by the sign of the product $(R_1 - R_2)$ $(\kappa_1 - \kappa_2)$, where R_1 and R_2 are the radii of the solute and solvent atoms, respectively.

When $(R_1 - R_2)(\kappa_1 - \kappa_2) > 0$, i.e., when the atoms with the larger radius have the lower compressibility coefficient, the deviations from linearity must have the positive sign, i.e., the linear dimensions of the solid solution (its lattice constants) must be larger than those computed by Wegard's rule. When the atoms with the larger radius have the larger compressibility coefficient (the case most frequently encountered), the deviations should have the negative sign.

Many theoretical and experimental investigations have been devoted to diffusion in solids. Their result has been establishment of the essential part taken by diffusion phenomena in sintering, re-crystallization, "relaxation," and chemical reactions of crystalline solids and in certain other important processes in which they undergo transformation, in earlier treatments of which inadequate attention or no attention at all had been devoted to diffusion.

Consequently, study of diffusion in solids is of great theoreti-cal and practical importance. The basic tasks of this study are to ascertain the mechanism and kinetics of diffusion, the influence that it exerts on various factors (the structure of the solid, the tem-perature of the process, the concentration of the diffusing element, and so forth), and its effects on other phenomena that take place in solids.

In permitting us in many cases to ascertain the interaction

energy and mobility mechanism of elements in the crystal lattice, as well as the nature of their defects, study of diffusion is also of great importance for development of the theory of solids.

Certain problems related to diffusion cannot be examined with sufficient rigor within the framework of contemporary solid-state theory, and remain without exact solutions to this day. As a result, sharply simplified models of the true phenomena are still generally used in describing them. These problems include bulk diffusion in alloys, diffusion along crystal faces, surface migration of matter, diffusion complicated by chemical reaction, and certain others.

However, the information available on diffusion in solids at present time is adequate to illuminate the basic quanitative laws governing this process and to characterize the basic problems and trends in subsequent research on it.

Diffusion is migration of matter as a result of the chaotic motion of its particles governed by kinetic energy, or their directional motion as governed by concentration gradients or chemical potentials. In the latter case, diffusion takes place in the direction of lower concentration of the diffusing agent or higher chemical potential of the solvent. In practice, diffusion is frequently the result of a combination of both of these phenomena.

The diffusive processes that take place in solids are distinguished by wide variety. We distinguish, first of all, between self-diffusion and heterodiffusion in solids in accordance with whether a crystal lattice is subject to migration of its own elements (atoms) or that of foreign atoms, ions, and so forth.

Quantitative investigations were started much earlier for hetero-diffusion than for self-diffusion; prior to the work of Kheveshi [sic] [75, 76], study of the latter was made difficult by the impossibility

of labeling atoms of a given substance and thus tracing their motion in the crystal lattice. At the present time, the tagged-atoms method can be used for quantitative study of self-diffusion on a large scale.

In accordance with the manner in which the atoms, ions, or molecules migrate, we distinguish bulk diffusion (diffusion taking place in the interior of the lattice), diffusion along faces and defects of the crystals (along "internal surfaces" of the solid), and surface diffusion (diffusion along the external surfaces of grains). The first of these has been most thoroughly studied, and the latter to a considerably lesser degree; as concerns diffusion along crystal faces ("internal surfaces"), only fragmentary information is available concerning it.

In the case of displacement of matter in a powdered granular mass, we also distinguish between external (between grain surfaces) and internal (intragrain) diffusion. In accordance with the direction of the diffusion flows and certain conditions of the process, we distinguish unidirectional (unipolar) diffusion, equilibrium (equal amounts in either direction) diffusion in the interior of the solid, counterdiffusion (simultaneous propagation of masses having different compositions in two opposite directions), and so forth.

There exist two states of the diffusion flow: steady and non-steady. In the steady state, the flow parameters (e.g., the concentration of the diffusing agent) do not vary in time at a given point, and as much material arrives in a given elementary volume per unit time as leaves it. Mathematically, this is written as follows:

$$D(\text{div grad})\, C = 0, \qquad (15)$$

where D is the diffusion coefficient and C is the concentration of the diffusing agent in the diffusion medium.

- 66 -

If diffusion is accompanied by chemical interaction between the diffusing agent and the diffusion medium, the phenomenon is severely complicated. Certain problems pertaining to this and examined in the papers by Wulis [77], Fishbek [78], Frank-Kamenetskiy [79] and other investigators will be elucidated below.

TABLE 11

Influence of Atomic Radius on Direction of Diffusion

1) Система	2) Минимальное расстояние r·10⁸ в см	3) Направление диффузии
Cu — Pt	Cu : 2,54	Pt : 2,78 4) Медь в платину
Cu — Zn	Cu : 2,54	Zn : 2,67 / 2,92 5) Медь в цинк
Fe — Ag	Fe : 2,54	Ag : 2,88 6) Железо в серебро
Au — Pb	Au : 2,88	Pb : 3,48 7) Золото в свинец
Fe — C	C : 1,50	Fe : 2,54 8) Углерод в железо

1) System; 2) minimum distance $r \cdot 10^8$ in cm; 3) direction of diffusion; 4) copper into platinum; 5) copper into zinc; 6) iron into silver; 7) gold into lead; 8) carbon into iron.

The question as to the direction or, more precisely, the preferential direction of diffusion, is worthy of attention. This question can be formulated somewhat differently, as follows: which of two contacting solids will be the solvent and which will be the solute, the diffusing agent?

Sen's rule [80], according to which the direction of the higher diffusion rate when two bodies are brought into contact will be in the direction of the body in which the smallest interatomic distance is larger, gives a first-approximation answer to this question.

The validity of this rule for atomic lattices is illustrated in Table 11.

The rate and, accordingly, the preferential direction of diffusion in ionic lattices also depends on the relationship between the charges and radii of the ions and on the related degree to which they

are polarized.

The diffusion mechanism, which is investigated in papers by numerous authors, is quite complex.

According to the first, simplest conceptions of it, which were formulated by Kheveshi [75], the diffusion process is effected by pairwise place-changing by neighboring lattice elements (atoms) during thermal agitation. On the basis of these conceptions, which were quite widely accepted in their time (particularly in studies of solid-phase reactions), and employing simple statistical reasoning, Graune [81] made an attempt to create a quantitative theory of thermal motion in solids.

Later, however, the concept of simultaneous place-changing by adjacent lattice elements as the only or basic phenomenon governing diffusion was rejected for a number of reasons. Principal among these was the fact that the concept excludes or ignores the actually quite real possibility of individual migration by an atom or ion irrespective of the migration of its neighbors. Further, the probability of simultaneous migration by two neighboring lattice elements is, of course, very low. Such migration requires either an instantaneous very severe deformation of the atoms (ions) that are changing places or displacement of the neighboring atoms (ions) to a distance equal to two atomic (ionic) diameters. Obviously, such a severe lattice deformation at the points of exchange would involve a colossal increase in the lattice energy at these points. Finally, using the above conception of simultaneous exchange as a point of departure, it is difficult to account for the phenomenon of electrical conductivity in ionic crystals (since pairwise exchange cannot produce a resultant current in them) and certain other phenomena that are in fact observed.

The conclusion that direct place-changing between neighboring

atoms is highly improbable has been confirmed experimentally in the studies by Smigel'kas and Kirkendal [82] and Pines [83, 84] on diffusion in certain metals and alloys.

In 1923, as a result of a study of conductivity in salt crystals, Ioffe [85] advanced new conceptions for the mechanism of mass transfer in a crystal lattice; subsequently, these served as the basis for a highly fruitful quantitative theory of diffusion developed by Frenkel' [86].

At the present time, on the basis of the monumental work of Frenkel' and investigations by numerous other authors (see, for example, [87-89]), the process of diffusion in the crystal lattice may be represented as consisting of the following basic phenomena:

1) displacement of an element (atom) of the lattice from its regular position at a lattice point into an irregular position in an interstice ("dissociation" of bound atoms);

2) migration of the lattice element from a regular position to a regular position;

3) migration of the lattice element from a regular or irregular position to a vacant point of the lattice — a "hole" ("association" of dissociated atoms);

4) migration of vacant points ("holes") of the lattice (successive jumps by atoms or ions of the lattice from the regular positions that they occupy to other, nearby, unoccupied regular positions).

It is these phenomena — motion of "vacancies" and dissociated atoms — that govern diffusion and electrolytic conduction in crystals.

In principle, all of the mechanisms listed above for mass transfer in lattices are possible, as is direct place-changing by atoms or migration of atoms as a result of the construction of new super-
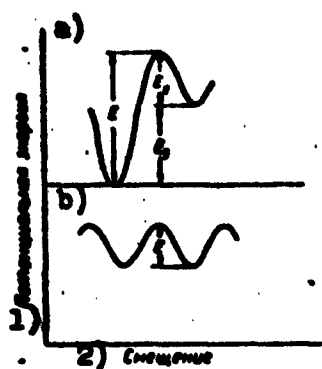
Fig. 17. Variation of potential energy on migration of atom: a) from lattice point into interstice; b) from interstice into next interstice. 1) Potential energy; 2) displacement.

ficial layers on the crystal (see below). This is confirmed by the appearance of the widest variety of changes in the crystal structure as a result of many cases of diffusion; in particular, we note the formation of the various types of solid solutions.

However, any one of the mechanisms may be dominant in each specific case. Let us compare them with one another.

As was indicated above, the part taken by direct place-changing is virtually negligible in diffusion processes.

The penetration of a dislocated atom into an interstice in the first or second variant of the diffusion mechanism involves outward displacement of the atoms about the new position of the atom in the interstice. This, the lattice becomes severely deformed in the neighborhood of a dislocated atom (see Fig. 16). This deformation requires a large expenditure of energy, composed of the energy difference E_1 between the interstitial and regular positions and the height E_2 of the additional potential barrier that must be overcome to move the atom from its regular position to the interstice* (Fig. 17). As a result of this deformation, however, the energy barrier that must be overcome by the dislocated atom on its subsequent migration into a new position (in the second variant of the mechanism) is lower than the barrier overcome on transition to the interstice from the normal lattice-point position (in the first variant), i.e., dislocated atoms possess elevated mobility.

The work of "hole migration," i.e., the work of kicking an atom

into a vacant point, thus vacating its original lattice-point position and subsequent substitution of the vacant point by an atom that jumps into it from another nearby lattice point, does not involve displacement of lattice atoms and is therefore considerably smaller than the work of dislocation of an atom.

If an atom in a superficial layer of a crystalline solid goes only to the surface of the body but not into the gaseous phase as a result of its vaporization, the result may be the appearance of a new surface layer. The place vacated by the atom that has migrated to the surface may be taken by one of the atoms of the same (surface-adjacent) layer or an internal layer near it. The vacated position may be replaced by some atom of the same or the next inward layer. In this case, vacancies ("holes") are again forming and then migrating.

The work required to move an atom to the surface is rather large. However, the energy barrier to be overcome here is smaller than the one that must be overcome in moving an atom to the gaseous phase or in its migration into an interstice.

The modern theory of solids enables us to evaluate the activation energy of diffusion for its various mechanisms. Such calculations indicate, firstly, that the heat of activation is larger for direct exchange than in dislocation to an interstice, and that the latter is larger than the heat of evaporation to the surface.

According to the calculations of Huntington and Seitz [90], the activation heat of self-diffusion of copper is, for example, 400 for direct exchange, 230 for dislocation, and 64 kcal/g-atom for the "hole" mechanisms; according to experimental data, this quantity amounts to about 50 kcal/g-atom.

Let us note that heterodiffusion in crystalline solids is intimately related to the phenomenon of self-diffusion. In principle,

- 71 -

the mechanisms of the two processes are identical. However, as has been established by experiment, the activation energy of the self-diffusion process is always larger than that of heterodiffusion in a given lattice.

Simultaneously with the appearance of "holes" due to dissociation of atoms, holes also vanish in the lattice due to the so-called recombination: encountering "holes" that are migrating in the lattice during their own migrations among the interstices, the dissociated atoms occupy their positions, thus eliminating defects of both types (dislocated atoms and "holes").

The probability that a wandering atom will encounter a "hole" in the course of 1 sec is obviously proportional to the number of migrating dissociated atoms and "holes" per unit volume.

Since the appearance of either type of defect is governed by thermal motion, the number of defects will increase with increasing temperature in accordance with a certain law.

Proceeding from the laws of statistical physics, Frenkel' [86] proved that a certain equilibrium concentration of the two types of defects corresponds to each temperature; at this concentration, the numbers of elementary dissociation and recombination events taking place per unit time are the same. The number of vacancies ("holes") N_v in the crystal may be expressed for any temperature T by the equation

$$N_s = N_f e^{-\frac{U}{kT}}. \tag{16}$$

where N_u is the total number of lattice points, $\underline{k}$ is Boltzmann's constant, U is the energy of formation of the vacancies.

As regards its order of magnitude, the quantity U is closely similar to the latent heat of evaporation, from which, among other things, it follows that the "hole concentration" in the crystal is a

quantity of the same order as this crystal's saturation vapor con-
centration in the surrounding space at the same temperature.

Let us dwell briefly on the problem of the latent energy of
deformation of a real crystalline solid. As we know, this energy
(which varies from a few calories to several hundred calories per
gram-molecule), as well as the nature of and laws governing its liber-
ation during roasting, depend on the nature and relative number of
the defects present in the solid.

According to the conceptions of Mott [92], which are most
widely accepted at the present time, the latent energy may be accum-
lated in groups and collections of dislocations that have been held
up at obstacles and be linked with vacancies and dissociated atoms.
Above we discussed only isolated dislocations. It should be noted
that the energy of formation of a certain number of isolated disloca-
tions is very small as compared with the energy of formation of a
dislocation group, since in the latter case it is necessary to do :
work against the forces repelling them from one another.

The following processes, a partial description of which was
given above and which take place on heating of a crystalline solid,
are of interest in connection with the problem being considered:

1) elimination of vacancies (as a result of their diffusion to-
ward the boundaries of blocks and disappearance at these boundaries),
which is accompanied by evolution of part of the latent energy and an
increase in the density of the solid;

2) disappearance of dislocated atoms with the evolution of
energy; this results in no essential change in the density of the
solid;

3) redistribution of the dislocations in groups, which is accom-
panied by a reduction in the system's energy margin;

- 73 -

4) dispersion of dislocation groups into isolated dislocations, which is accompanied by liberation of energy.

Fig. 18. Evolution of latent energy (I), variation of resistivity (II) and hardness (III) in annealing of copper [93, 94].
1) $\Delta\rho$ [10^{-6} ohm-cm]; 2) $\Delta\rho$, mw.

Determining the activation energy of the process taking place in the solid during its annealing, and observing the changes that take place in the solid's density, conductivity and hardness during this process, we may, to a certain degree, draw inferences as to its nature. Klerbro [93, 94] observed, e.g., for copper, that the liberation of latent energy, which

is accompanied by a drop in the resistivity and hardness of the solid (Fig. 18), is associated with recrystallization of copper in the temperature interval studied.

It may be assumed that the disappearance of vacancies and the liberation of energy associated with this disappearance take place at lower temperatures in copper than would be indicated by Klerbro's experiments.

In heating of nickel, liberation of latent energy takes place in three stages (Fig. 19). In the first, low-temperature stage, it is not associated with a change in hardness, but is accompanied by a drop in the metal's resistivity. Such phenomena may be governed chiefly by the disappearance of vacancies. A subsequent uniform evolution of energy (second stage) in the temperature region extending approximately from $300°$ to $550°$ may be associated with motion and redistribution of dislocations and a decline in the energy of their interaction.

In this temperature interval, the dislocation-disappearance process may proceed by annihilation of dislocations having opposite signs. The third, high-temperature peak in the evolution of latent energy corresponds to the recrystallization temperature of nickel and is accompanied by a sharp drop in hardness (attesting to a decline in grain fragmentation and substructural changes), a small drop in resistivity, and a considerable increase in density; this peak may be associated with decay of dislocation groups into individual dislocations, probably with a simultaneous decrease in the number of dislocations (and a corresponding increase in density).

Obviously, study of the processes in which the latent energy is absorbed and liberated in the various crystalline phases of the defect structure, in combination with observation of the processes in which the above properties vary, may provide valuable information concerning the transformations to which these phases are subject.

Let us turn our attention to the general laws governing the diffusion process.

In the steady state of the diffusion flow, the quantity of matter in moles that diffuses through a layer having an area dS $[cm^2]$ during a time $d\tau$ sec is determined after Fik from the equation

$$dQ = - D\frac{dC}{dx}dSd\tau. \qquad (17)$$

Here, dC/dx is the concentration gradient of the diffusing agent in the diffusion layer in moles/cm; D is the diffusion coefficient in this layer in $cm^2/sec.$*

The minus sign before the D indicates diffusion toward lower concentrations (negative increment).

Obviously, for $dC/dx = -1$, $dS = 1$ and $d\tau = 1$,
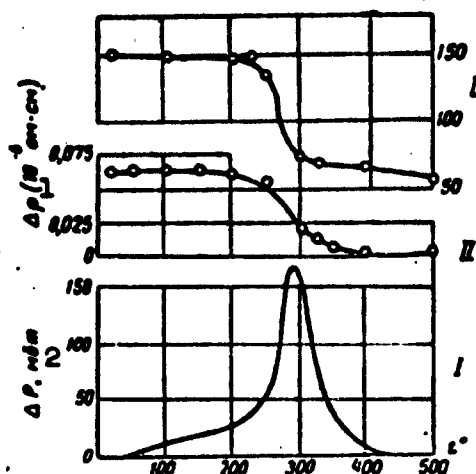
$$D = dQ.$$
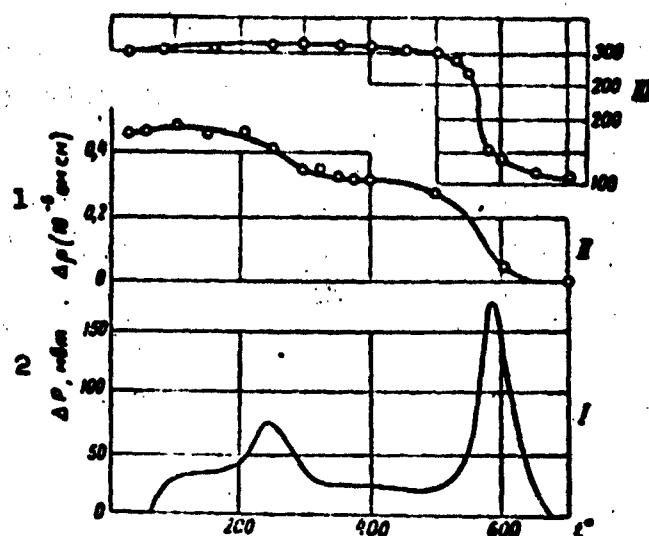
Fig. 19. Liberation of latent energy (I),
variation of resistivity (II) and hard-
ness (III) in annealing of nickel [93, 94].
1) $\Delta\rho$ [10^{-6} ohms-cm]; 2) ΔP, mw.

i.e., the diffusion coefficient expresses the quantity of matter that
diffuses in a unit time through a unit area of the diffusion layer
with a concentration gradient of unity. The value of D depends on
the properties of the diffusing agent and the diffusion medium, the
direction of the flow (diffusion anisotropy) and the conditions of
diffusion (the temperature of the process, the concentration of the
diffusing agent, and so forth).
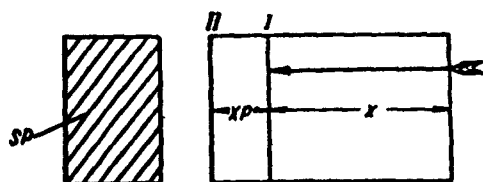
Fig. 20. Diagram of diffusion
process (illustrating deriva-
tion of second expression of
Fik's law).

In the nonsteady state of the
flow with concentration changes of
the diffusing agent in the diffu-
sion layer, this change may be des-
cribed on the basis of the follow-
ing considerations.

The amount of matter passing
by diffusion through plane I during a time dτ into a layer of volume
dS·dx that is bounded by planes I and II, which are separated from
one another by a distance dx (Fig. 20) is

$$dQ_1 = -\left[D\left(\frac{dC}{dx}\right)\right]_x dS\, d\tau, \tag{18}$$

while the quantity of matter leaving this layer through plane II during the same time is

$$dQ_2 = -\left[D\left(\frac{dC}{dx}\right)\right]_{x+dx} dS\, d\tau. \tag{19}$$

The accumulation of the diffusing substance in the volume under consideration during the time $d\tau$ is

$$dQ = dQ_1 - dQ_2 = \left\{\left[D\left(\frac{dC}{dx}\right)\right]_{x+dx} - \left[D\left(\frac{dC}{dx}\right)\right]_x\right\} dS\, d\tau = \\ = d\left[D\left(\frac{dC}{dx}\right)\right] dS\, d\tau. \tag{20}$$

The change in the concentration of this material in the volume $dSdx$ is

$$dC = \frac{dQ}{dS\, dx} = \frac{d}{dx}\left(D\frac{dC}{dx}\right) d\tau \tag{21}$$

and the rate of change in the concentration is

$$\frac{dC}{d\tau} = \frac{d}{dx}\left(D\frac{dC}{dx}\right). \tag{22}$$

In cases where diffusion in more than one dimension is possible, it is more correct to write

$$\frac{\partial C}{\partial \tau} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right); \tag{23}$$

the same applies for two dimensions:

$$\frac{\partial C}{\partial \tau} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right), \tag{24}$$

and for three dimensions

$$\frac{\partial C}{\partial \tau} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right). \tag{25}$$

In the simplest case, in which the diffusion coefficient does not depend on concentration, Equations (23-24) assume the following respective forms:

$$\frac{\partial C}{\partial \tau} = D\frac{\partial^2 C}{\partial x^2} \tag{26}$$

(second expression of Fik's law),

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} \tag{27}$$

and

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} + D \frac{\partial^2 C}{\partial z^2} \tag{28}$$

this last equation may also be written in the form

$$\frac{\partial C}{\partial t} = D \nabla^2 C \tag{29}$$

or

$$\frac{\partial C}{\partial t} = D (\mathrm{div\ grad}) C. \tag{30}$$

All this is valid for an isotropic medium.

In the case of diffusion anisotropy, which is frequently encountered in practice [88], we should write instead of Equation (28)

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \tag{31}$$

(we note here that the diffusion coefficient, which is a second-order tensor, is independent of temperature in cubic crystals).

Using the appropriate transformations, we may also express Equation (28) in spherical polar coordinates or cylindrical coordinates [88].

In the case, for example, of spherically symmetrical diffusion, the solution takes the form

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right]. \tag{32}$$

where r is the radius of the sphere.

Substituting $Cr = U$, we easily obtain

$$\frac{\partial U}{\partial t} = D \frac{\partial^2 U}{\partial r^2} \tag{33}$$

and then, employing the techniques set forth for "two-dmensional" cases, arrive at analogous solutions.

For certain cases, rigorous solution of Equations (32, 33) involves considerable difficulty, and none has as yet been found. For many cases that are of practical importance, however, References [89, 95, 96] give a solution that makes it possible to find the concentration C of the diffusing agent in the diffusion layer for these cases as a function of x and τ.

An important quantity in determining the diffusion rate is the diffusion coefficient D which, as was noted earlier, depends in turn on a number of factors. Basic among these are the structure of the solvent and solution lattices, the temperature of the process, and the concentration of the diffusing agent in the diffusion medium.

All other conditions the same, the value of the diffusion coefficient is antibatic to the solubility of the solid and is found to be very small in cases, for example, of self-diffusion ("unlimited solubility"). This stems from the fact that the work of loosening the lattice, which makes diffusion possible, is smaller when the atoms of the dissolved substance and the solvent are of different species; here there is a smaller difference between the degrees to which the lattice is disturbed in the normal and transitional states of the solute or, accordingly, before diffusion and in the diffusion process.

The work of opening the lattice increases and the diffusion coefficient diminishes with increasing melting point of the solvent - which, as we know (Chap. 1, §2), is associated with the compactness and strength of the lattice.

Polarization of the ions, which was referred to earlier, exerts a strong influence on the diffusion coefficient in ionic lattices. The considerable drop in the energy necessary to impart mobility to an ion is accounted for, as it occurs on polarization, by the Frenkel' ionic-conductivity theory [86]. The greater the polarization of a ca-

tion, the greater, naturally, will be the possibility of diffusion
in the lattice.

It was established some time ago by Kheveshi [75] that

$$D = Ae^{-\frac{Q}{RT}}.$$ (34)

where the coefficient A, which is frequently written D_0, is a so-called
temperature-independent factor (which is not absolutely true) or the
pre-exponential factor, is formally equal to the diffusion coefficient
at infinite temperature (when the resistance to diffusion is zero) and
Q is the heat of activation of diffusion (or the energy of "opening"
the lattice), so named by analogy with the heat of activation of a
chemical reaction.

This equation, which is analogous to the familiar Arrhenius
equation for the rate of a monomolecular reaction, is valid for all
conditions and mechanisms of diffusion that have thus far been inves-
tigated.

Identification of the coefficient A = D_0 with the diffusion co-
efficient at T = ∞, as proceeds formally from Equation (34), does not,
however, have any physical significance in actuality and does not re-
solve A from its dependence on the factors that determine it. Many
authors link the parameter A with the frequency of the atomic vibra-
tions.

According to Frenkel' [44, 45, 86, 97], the quantity A may be
determined if we know the average distance δ between neighboring
equilibrium positions (which may be assumed equal to the distance
between neighboring atoms) in the lattice and the duration τ_0 of the
atom's natural-vibration period (which is the reciprocal of the max-
imum frequency N of the vibrations); for the majority of substances,
the values of δ and τ_0 are known.

By analogy with the Einstein theory of Brownian movement, the

diffusion coefficient

$$D = \frac{1}{6} w\lambda,$$

(35)

where $\underline{w}$ is the average velocity of displacement of the atoms.

Assuming that

$$w = \frac{\lambda}{\tau},$$

(36)

(where τ is the average duration of the vibrations of an atom about a given equilibrium position), we obtain

$$D = \frac{1}{6} \frac{\lambda^2}{\tau},$$

(37)

and, since according to Frenkel' [44] $\tau = \tau_0 e^{Q/RT}$ (which is admittedly not altogether accurate, since it assumes that the vibrations of the atoms are statistically independent of one another), then

$$D = \frac{\lambda^2}{6\tau_0} e^{-\frac{Q}{RT}}$$

(38)

or, in other words,

$$A = \frac{\lambda^2}{6\tau_0}.$$

(39)

Other expressions for A as a function of the parameters determining it are also known, e.g., that of Polyani and Wigner [98]:

$$A = \frac{2\lambda^2 \nu}{RT} Q,$$

(40)

instead of Equation (38), which takes into account the dependence of A on temperature (more properly on Q/T), and the Deshman and Langmuir [99] equation, which differs only slightly from Formula (40):

$$A = \frac{\lambda^2}{Nh} Q,$$

(41)

where N is Avogadro's number and $\underline{h}$ is Planck's constant.

Detailed analysis of these and certain other expressions defining the value of A and comparison of these expressions with experimental data are available in the literature [100 and others]. Here we

note only that Equation (34), in which the value of the coefficient A is proportional to δ^2, but depends in a complex manner on the nature and magnitude of the bonds between lattice elements, remains in force for any diffusion mechanism.

The Frenkel' theory, which appeared, as we know, toward the end of the development of experimental research on the self-diffusion process, did not reveal any functional relationship between the quantity Q — the heat of "opening" of the crystal lattice or the weakening of the bonds between its elements — and any parameters of the solid. Only recently, in the studies of Dekhtyar, Krivoglaz and Smirnov and certain other authors were any well-based attempts made to find a link between the quantity A and the nature and magnitude of the interatomic bonds in metals and alloys.

Normally, Q is determined experimentally from the slope of a straight line constructed in the coordinates ln D and 1/T (see Chap. 7).

According to Equation (34), the dependence of ln D on temperature is linear, as has been observed by many investigators [see 88, 89, 101]. In actuality, the activation energy of diffusion does not remain constant with varying temperature in many cases, and the dependence of D on temperature is more complex than would follow from Equation (34). Strictly speaking, diffusion systems may be classified into three groups in accordance with the various types of influence that temperature exerts on the diffusion coefficient:

a) those subject to a simple exponential law as given by Equation (34);

b) those described by equations linking D with T and incorporating two temperature-independent exponential terms, and

c) those not subject to any type of simple law linking the dif-

fusion coefficient with temperature (i.e., those characterized by highly complex dependences of D on T).

In the general case, Equation (34) may characterize the relationship between D and T only in first approximation, and then only in a relatively narrow temperature interval [78, 102, 103, and others].

In examining this problem as it applies to metals, Dekhtyar [104] showed that even in the simplest possible case (with the diffusion mechanism unchanging), thermal expansion of the solid at elevated temperature must result in a drop in the heat of diffusion. According to Dekhtyar, $Q_T = Q_0(1 - KT)$, where Q_0 and Q_T are the heats of diffusion at absolute zero and at T^o, respectively, and K depends on the thermal-expansion coefficient, the compressibility coefficient, and the atomic volume of the solid.

The diffusion process in alloys cannot be characterized by any single value of the activation energy: in this case, different diffusing atoms of the same species but having unlike environments of nearby atoms, overcome potential barriers of different heights, the formation energies of holes are different at different lattice points, and so forth.

Krivoglaz and Smirnov [103, 105, 106] showed in their development of a theory for the diffusion of atoms in alloys that for both disordered and particularly for ordered solid solutions, ln D does not depend linearly on 1/T. Transition of the solution from the disordered to the ordered state should be reflected on the temperature curve of the diffusion coefficient. If ordering represents a phase transition of the second kind, the diffusion coefficient varies continuously, while the curve showing the dependence on 1/T has a break at the transition temperature. If, on the other hand, the transition into the ordered state is a phase transition of the first kind, a stepwise

change occurs at the transition temperature not only in the energy of activation, but also in the diffusion coefficient itself. In the ordered state near the transition temperature, the deviations of the above relationship from the linear should be particularly marked.

In spite of all this, ln D is most frequently found to be a linear function of 1/T in experiments. This is accounted for by the fact that in a small temperature range (of the order of 300°), outside of which determinations of the diffusion coefficient normally do not take place, the curve of this relationship can be approximated by a straight line with a certain degree of accuracy. For example, the change in the heat of diffusion in metals is, according to Dekhtyar [104], 1000 cal/g-atom in this temperature interval; this is within the limits of error of ordinary diffusion-heat determinations.

Naturally, measurements taken over a wider temperature range or under conditions that make it possible to employ particularly accurate methods for determining the diffusion coefficient (e.g., methods based on observation of vibration damping in a specimen of alloy [107]) show a nonlinear relationship for the logarithm of the diffusion coefficient as a function of temperature.

Very frequently, the diffusion- coefficient value is a function of the concentration of the diffusing (dissolved) agent in the diffusion medium (solvent)*. This dependence becomes particularly marked at high solid-solution concentrations approaching the solubility limit of the diffusing agent.

Since D may vary quite considerably as a function of concentration, in some cases through a factor of one thousand [108], the use of Equation (34) in the case of dependence of D on C can give only "average" values of the diffusion coefficient and may lead to quite considerable errors in determining the coefficient $A = D_0$ and the heat of

diffusion.

In this case, the kinetics of diffusion are expressed by Equation (23) for which solutions now exist for many types of systems.

According to Boltzmann [109], solution of Equation (23) for mutual diffusion in plates of two materials that are in contact with one another may be given by the following equation if we assume that $C = f(x/\tau)$:

$$D_{(C=C_1)} = \frac{1}{2\tau}\frac{dx}{dC}\int_{C=C_1}^{C=C_1} x\,dx. \qquad (42)$$
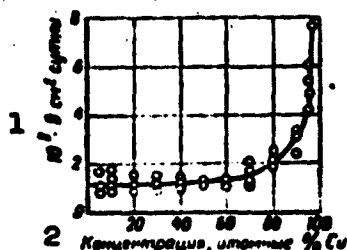
Fig. 21. Diffusion coefficient of copper as a function of its concentration in the Cu-Ni system. 1) $10^5 \cdot D$ [cm^2/day]; 2) concentration, atom-% of Cu.

D may be determined as a function of concentration from Equation (42) by graphic integration.

Taking advantage of this, Matano [108] found the diffusion coefficient as a function of concentration for a number of metallic systems. The experimental data of Matano (21, 22), Kurdyumov et al. [110] and other authors indicate that D is a complex function of the diffusing-agent concentration in the diffusion layer. This function assumes different characters in different cases. Frequently, the variation of D as a function of concentration is different in different areas on a given concentration diagram [88]. Sometimes an extremely insignificant change in concentration exerts a strong influence on the diffusion coefficient. In the report by Kurdyumov et al. [110], for example, it was established that the addition of a small quantity (less than 4.5 atom-%) of carbon to γ-iron considerably reduces the activation evergy of self-diffusion for iron and reduces the preexponential multiplier of Equation (34) by several orders of magnitude.

Gertskriken and Dekhtyar [111] and other investigators have ob-

served that small quantities of additives to the solvent exert considerable influence on the coefficient of diffusion. In many cases, contemporary theory of solids [87, 112] enables us to account for and even predict the nature and intensity of this influence on the basis of comparison of the lattice-element interaction energies (those of atoms, ions and molecules) in the system and analysis of the processes that take place in it.

Diffusion (migration) of matter in the superficial layer of a solid is of considerable interest, and has recently attracted the interest of many authors [97, 113-117 and others].

The phenomenon of surface migration was demonstrated by the studies of Pol'-mer et al. [113-115] on the basis of studies of the growth and solution of single crystals. Subsequently, this effect was established and studied for a number of systems by observing the condensation and aggregation processes of continuous films on the surfaces of crystalline solids. Finally, photoelectric and thermionic methods based on observation of the variation

Fig. 22. Diffusion efficients of substances as functions of concentration in the systems 1) Au-Ni; 2) Au-Pd; 3) Au-Pt. A) $10^{10}D$ [cm^2 sec^{-1}]; B)concentration, atom-% of Au.
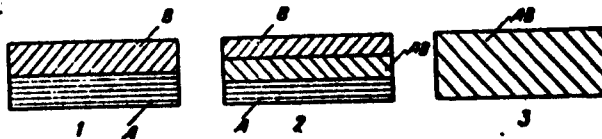
Fig. 23. Chemical reaction between two ideally ground tablets, accompanied by diffusion in the product layer. 1) At initial point in time; 2) during reaction; 3) at completion of reaction.

of thermionic and photoelectric currents, which are affected when the

surfaces of crystals are coated by a film of migrating atoms, have been applied successfully for study of this phenomenon [88, 116, 117]. This has made it possible to obtain new data concerning superficial diffusion.

Nevertheless, information available on it is still rather limited. It is known, however, that if surface diffusion occurs, it usually occurs much more readily than bulk diffusion or grain-boundary diffusion along the "internal surfaces" of the solid. Comparison of the activation energies for these three forms of diffusion in such cases leads us to the conclusion that

$$Q_{surf} < Q_{gr.\ bdry} < Q_{latt(bulk)}.$$

Accordingly, all other conditions (temperature, etc.) the same,

$$D_{surf} > D_{gr.\ bdry} > D_{latt(bulk)}.$$

It has also been established that in much the same way as the bulk-diffusion coefficient of the lattice, the surface-diffusion coefficient depends on temperature and surface concentration.

The elevated mobility of the surface particles of a crystalline solid is readily understood on the basis of its structure. As we know, the surface layers of real crystals are characterized by inconstancy of the coordination number of the lattice structural elements (atoms, ions, molecules), the distances between its points, and the bonding angles between its structural elements. As a result, particles of the solid that are at its surface are the least stable. This renders readily understandable the possibility not only of relatively intensive surface diffusion, but also of particle displacements from one crystalline solid into another at the points of contact between them.

In a chemical reaction between crystalline substances, diffusion of one of the reagents toward particles of the other through the layer

of product that forms and grows during the reaction is of great importance.

In this case, the rate of the process may depend on the rates of both the diffusive and chemical interactions.

If we speak here of the interaction between two ideally mated plates (tablets) of the reagents A and B, the pattern of the process for the simplest case may be represented by Fig. 23. In a real powdered mixture, the interaction process is considerably more complicated. Quite naturally, it takes place at the surfaces of the reagent grains only at the very beginning of the interaction (assuming a reaction time close to zero). Completion (continuation) of the chemical reaction then requires mass transfer: particles of one of the reagents must displace toward the zone of their interaction with the other reagent through the medium separating them, traversing successive zones of external (between grains) and internal (in grains) diffusion. Here, the internal diffusion usually takes place in equal volumes in either direction, and the product-formation rate corresponding to it is practically uniform over the entire grain surface of the reagent that it covers [118, 119].

Two elementary and fundamental variants of such equal-access, symmetrical diffusion and mass transfer that are not mutually exclusive are possible [120].

In the first of these (Fig. 24a), particles of the migrating reagent move to the surface of a layer of crystalline product covering the grains of the other reagent through zones of direct contact between the grains. Then the particles move across the surface, enveloping it completely, after which they diffuse with "equal access" toward the unreacted part of the "coated" reagent through the layer of crystalline reaction product.
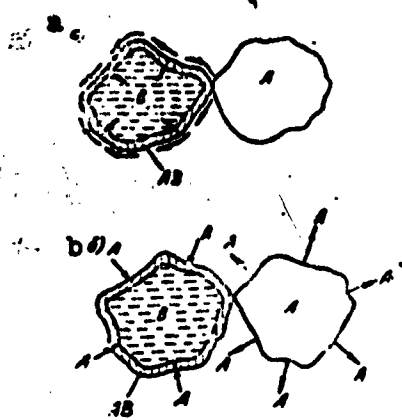
Fig. 24. Diagram showing migration of particle A toward B during their chemical interaction in a powdered mixture of A + B. a) Through zones of direct contact; b) by external diffusion.

In the second variant (Fig. 24b), particles of the migrating substance are in some way dislodged from the positions that they occupied in its grains, travel the distance separating them from the grains of the second reagent (external diffusion), and then, as in the first variant, traverse a layer of crystalline reaction product (internal diffusion).

In either case, the kinetics of the process are further complicated if the rates of diffusion and chemical reaction have commensurate values, and particularly if diffusion is accompanied by a concurrent reaction in the diffusion layer.

All of this has its effects on the kinetics of diffusion-chemical processes in crystalline mixtures, which, in certain cases, becomes very complex.

§2. RECRYSTALLIZATION

Sintering is one of the most important of the phenomena that unfold when mixtures of crystalline solids are heated. It may affect both the rate of the reactions between the solid substances and the properties of the products obtained from them. This is why considerable attention is devoted to the sintering process in papers on the chemistry of solids.

In the literature, we encounter the widest variety of inferences concerning the external manifestations of this process, concerning its essential nature, its qualitative laws and the influence that it exerts on other processes that take place when crystalline mixtures are heated.

There are at least ten theories of the sintering process (due to Frenkel', Bal'shin, Ivensen, Pines, Fedorchenko, Jones, Sauerwald, Kingery, Kushchinskiy, Tschebyatovskiy, et al.). None of these has as yet been definitely proven valid. This is a consequence of the complexity of the process under consideration and the inadequacy of the study that has been devoted to it.

Papers that have been published on the subject of sintering during the last several years by Soviet and foreign investigators nevertheless enable us to formulate with a certain amount of succinctness certain basic propositions that relate to it and are of importance to the chemistry of solids. These points can be accounted for on the basis of general premises and with the aid of the generalized methods of thermodynamics, and the causes of certain contradictions in various works on the theory of sintering become clearer in the process.

The decrease in the solid's external dimensions (i.e., "shrinkage") on heating and the corresponding decrease in its porosity and increase in its apparent density may serve as the external criterion for the sintering process in a porous and particularly in a disperse crystalline solid.

Sintering of a powder usually begins with "welding together" of the grains at the points of contact.

The essence of the sintering phenomenon consists in spontaneous filling of the free space within and between the grains with matter (as a result of the elevated mobility of the lattice elements at sufficiently high temperatures).

This is naturally accompanied by a change in the total and contact areas of the grains; the former diminishes and the latter increases.

The sintering process is also attended by recrystallization of the grains, a decrease in the number of lattice defects (relaxation),

and relief of existing stresses in the contact zones of the material.

All of this affects not only the mechanical and thermal properties of powdered solids, but also the sectional areas of the diffusion flows, the values of the diffusion coefficients and diffusion rates, the "internal" and surface activities of the grains, and the rates of reactions in the powdered mixtures.

Industrial and research practice draw a distinction between sintering proper, or sintering in the solid phase, which takes place in the absence of liquid, and so-called liquid sintering.

The natures of these processes and the qualitative laws governing them are different.

It is also necessary to distinguish sintering of pressformed powders, which possess a relatively large initial contact surface and low porosity, and sintering of unpressed, loose-poured powders, where the average intergrain distance has the same order as the grain diameter (see Ch. 4 §4) and porosity sometimes exceeds 90%.

Pressformed powders are used chiefly in powder metallurgy, while unpressformed powders are used chiefly in the chemical industry, in adhesives technology, and in pyrometallurgy.

If we consider the sintering process from the general premises of thermodynamics, reduction of the system's thermodynamic potential should be regarded as its motive force. Since the resultant of the forces acting on any superficial particle is directed toward the interior of the body (grain), there will always be a tendency toward reduction of surface area. The decrease in the total grain surface area during the sintering process results in a decrease in the surface energy of the system, and, consequently, in its total energy (energy is expended in overcoming internal-friction forces during the diffusion process).

It follows from the above that the motive force of the sinter-
ing process in a disperse solid will be larger the larger its surface
energy. Among other things, this can be cited to account for the
antibaticity of sintering to grain size in the heated material that
is observed in practice [121]: fine-grained powders sinter faster
than coarse-grained powders.

Since the internal pores of the crystal form its "internal sur-
face," their overgrowing process also results in a drop in the sys-
tem's thermodynamic potential.

Since the specific surface area of a pore is inversely proportional
to its radius, the motive force of the overgrowing process of small
pores will be stronger than that for large pores when pores of differ-
ent sizes are present in the solid. Accordingly, small pores overgrow
more rapidly provided that the difference in the resistance to the
pore-reduction process for pores of various sizes (due, for example,
to the varying increases in gas pressure inside them) does not affect
the pattern. Here, it is possible for the volume and number of small
pores to diminish at the expense of an increase in the volume of the
large pores (an effect frequently observed in practice [122]), since
this also results in a drop in thermodynamic potential.

The groundwork for the development of a quantitative theory of
the solid-phase sintering process was laid some time ago in the stu-
dies of Frenkel' [97]. According to Frenkel', sintering of crystal-
line solids occurs as a result of their "viscous friction," which is
analogous to that observed in liquids; the mechanism of this flow is
diffusive and can be reduced to directional displacement of "holes."

From the standpoint of Frenkel', the sintering process can be
broken down into two stages in time:

1) coalescence of particles, which results in the disappearance

of open pores (cavities) and the formation of noncommunicating closed pores of one shape or another (spherical in the simplest approximation) and

2) a reduction in the volume of closed pores under the influence of surface-tension forces.

The first stage of the process unfolds at a constant rate, being dependent only on the surface tension σ and viscosity μ of the medium surrounding the pore:

$$\frac{da}{d\tau} = \frac{3}{4}\frac{\sigma}{\mu}.$$

(43)

where a is the pore radius and τ is time. The area of the contact surface between the particles is proportional in this stage to the time of the process.

The time for total closing of the pores is determined from the equation

$$\tau = \frac{4}{3}\frac{\mu a_0}{\sigma}.$$

(44)

where a_0 is the initial radius of the pore at $\tau = 0$. The time for "full coalescence" of two sperical particles is of the same order of magnitude as the time for closing pores of the same radius.

In the second stage, the rate of the process diminishes continuously as a result of the inhibiting effect of the gas enclosed in the pores.

When the gas pressure in the pores, which is increasing continuously in accordance with the equation $P = P_0(a_0/a)^3$ as a result of the decrease in their volume, is equal to the capillary pressure, i.e., at $P = P_0(a_0/a)^3 = 2\sigma/a$, where P_0 and P are the gas pressures in the pore at the start of the process at $\tau = 0$ and at the point in time in question, the process ceases.

Here, the limiting (maximum) pore radius is

$$a_{min} = \sqrt{\frac{P_0 a_0^3}{2\sigma}}$$

According to Frenkel', the second stage of the process may, in actuality, occupy a very short time and result in almost complete disappearance of the pores.

The Frenkel' theory, which has played an extremely important role in the development of sintering theory, nevertheless disregards the following circumstances observed in the unfolding of this process in real powdered solids:

a) the considerable variety in their granulometric composition;

b) the presence within them of pores having various sizes and shapes and the possibility of varying behavior from different pores of the same solid;

c) the differences in the viscous flows of the crystalline and liquid bodies.

As was shown by studies [83, 121-124 and others], the influence of these factors on the sintering process is quite considerable. Among other things, sintering takes different courses in powdered solids of different granulometric compostions; the mechanism and kinetics of "viscous flow" are not the same in solids and liquids, and so forth.

On the basis of the studies by Pines and other investigators, it may be assumed at the present time that the sintering process in a real powdered solid is effected chiefly as a result of volume diffusion and partly as a result of surface diffusion.* The mechanism of "cold" sintering, which takes place in the absence of a liquid phase, thus reduces to redistribution of material in the solid by directional self-diffusion.

An interesting question is that as to directional displacement of atoms in the sintering of granules, which results in merging of

their pores, fusion of grains, etc. Since the motive force of the diffusion process is the concentration difference (or, in a broader sense, the chemical-potential difference), it is natural to assume that directional displacement and, consequently, sintering take place with different concentrations of the atoms or vacancies, as the case may be, at different points in the volume of the solid.

Actually, as noted by Pines [83], the "equilibrium vacancy concentration" cannot be uniform at different points in the volume of a porous solid or in a solid having internal surfaces, or in a continuous uniform body of irregular shpae whose surface does not correspond to the free-energy minimum.

If, for example, there is at the center of a body of radius R a pore of radius a $\ll$ R, in much the same way as occurs with the equilibrium vapor pressures above surfaces of different radii, the equilibrium vacancy concentration C_a near the pore will be higher than the equilibrium vacancy C_0 given by Equation (16) at the surface of a sufficiently large crystal, and by an amount

$$\Delta C = \frac{2a'}{a}\frac{V_0}{kT}C_0 \tag{46}$$

or

$$C_a = C_0\left(1 + \frac{2aV_0}{akT}\right). \tag{47}$$

Thus, a vacancy-concentration gradient in the solid is inevitable, and has as its consequence that a diffusion flow from the internal pores toward the outer surface of the body is established; vacancies are eliminated from the solid through its external surface. From this standpoint, sintering represents elimination of pores from the solid by self-diffusion.

Proceeding from these considerations, Pines [83] indicated that the rate of change of the pore radius during the sintering process

may be expressed by the equation

$$\frac{da}{dt} = -\frac{2s}{a^2}\frac{v}{kT}D,$$ (48)

where δ is a constant of the solid's crystal lattice.

According to this equation, the value of the rate is smaller by $(\delta/a)^2$ than the rate according to Formula (43) as proposed by Frenkel', who took the position that the relationship between the viscosity and self-diffusion coefficients conforms to the equality

$$\frac{1}{\mu} = \frac{D}{kT}\delta.$$ (49)

The total sintering time obtained from Equation (48) is

$$\tau = \frac{a_0^3}{v^3}\frac{kT}{6D_s}.$$ (50)

In the case of pores with a radius $a \cong 10^{-3}-10^{-4}$ cm, the value of the total sintering time according to this equation is 10^6 to 10^8 times longer than according to Equation (44).

Pines [183, 126] showed that experimental data on the duration of the sintering process for powders agreed considerably better with Equation (48) than with Equation (43), and that both sintering theories (the diffusion theory of Pines and the viscous-flow theory after Frenkel') lead to equivalent results if, instead of extending Relationship (49), which is peculiar to liquids, to crystalline solids we regard the following expression as holding for the latter: $1/\mu = D\delta^3/kTa^2$.

In connection with the occasionally encountered attempts to account for instantaneous or, more generally, very rapid reactions in crystalline mixtures by intensive sintering of these mixtures "after Frenkel'," it should be noted that the sintering time or coefficient of diffusion as obtained from Equations (44) and (49) are on the low side of the actual values by six or seven orders. Actually, the time required for full sintering, for example, of a pressformed metallic-

copper powder with a pore radius a = 10^{-3} cm and t = 900 to 1000 degrees is several hours [83].

Naturally, if the pore radius varies linearly in time in accordance with the Frenkel' equation (43) (and the change in its volume is proportional to the cube root of the duration of the process), the variation of pore volume over time is linear according to the Pines equation (48).
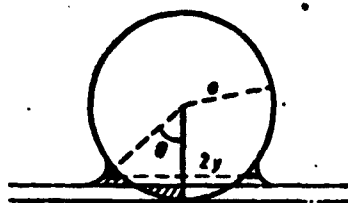
Fig. 25. Diagram of sintering of spherical particle to flat body.
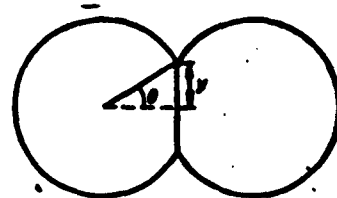
Fig. 26. Diagram of sintering of two spherical particles.

TABLE 12

Change in Number of Pores (in 0.0293-cm^2 section) During Sintering of Copper Powder in Hydrogen Medium

Размер пор 1 в см²	Температура 2 в град.	3 Продолжительность спекания в час.			
		1	10	100	1 000
9·10⁻⁸	900	1 654	1 423	850	757
	1 000	1 415	1 024	392	66
12·10⁻⁸	900	16	27	60	65
	1 000	65	73	93	113

1) Pore size in cm^2; 2) temperature in degrees; 3) sintering time in hours.

In fact, on manipulating Eq. (48), we obtain

$$a^2 da = -\frac{2\sigma\nu^2 D}{kT} d\tau,$$

from which the pore volume is

$$V = \frac{4}{3}\pi a^3 = K\frac{1}{\tau}.$$ (51)

If sintering of a spherical particle of initial radius $\underline{a}$ with a flat body (Fig. 25) or with an identical particle (Fig. 26) takes place, then, as was shown by Pines [83], the radius of the "contact circle" of the particle with the plane after a time τ has elapsed from the start of the process will be

$$y = \sqrt[4]{16\sigma\frac{D\theta^3}{kT}a\tau} = K\sqrt[4]{a\tau}$$ (52)

and the radius of the "contact circle" of one particle with the other will be

$$y = \sqrt[4]{8\sigma\frac{D\theta}{kT}a\tau} = K\sqrt[4]{a\tau}.$$ (53)

In accordance with the above, the relative change in the volume of a body containing N pores in 1 cm^3 is

$$\frac{\Delta V}{V_0} = 8\pi\sigma\frac{N\theta}{kT}D\tau.$$ (54)

Under practical conditions, the sintering process of the body may be severely complicated by the presence and nonuniform overgrowing of pores of different diameters.

The fact is that in accordance with what we said earlier (page 94), the vacancy concentration must be higher in the vicinity of the fine pores than near large pores. For relatively short distances between pores, this difference in vacancy concentration sets up a flow of vacancies from small pores toward larger ones or, in other words, a flow of atoms in the reverse direction. The result must be an increase in the volume of the large pores at the expense of overgrowth of the small ones. Here, the average pore diameter naturally increases. Experimental data are in good agreement with this proposition. Thus,

Rayns, Birchenoll, and Yuz [sic] [127] established that in sintering of copper powder in a hydrogen medium, the number of fine pores with diameters of $9 \cdot 10^{-8}$ cm^2 was reduced and the number of larger pores increased (Table 12).

Naturally, overgrowing of pores may result in a reduction of their number per unit volume of material and a corresponding retardation of the sintering process as a whole.

The phenomenon described above is complicated considerably when a gas is present in the closed pores. In this case, the sintering rate at any given moment of time is determined by the difference between the "negative" capillary pressure $P_k = \sigma/a$ drawing the pores together and the excess gas pressure:

$$P_i = P_0\left(\frac{T_1 a_0^2}{T_0 a^2} - 1\right),$$

which acts in the opposite direction; here, P_0 and P_1 are the respective gas pressures in the pores at the pressforming temperature T_0 and the sintering temperature T_1, which is higher than T_0; the pressure P_0 in the pores is equal to the pressure outside the pores during pressforming and sintering.

Obviously, three cases are possible in principle:

$$P_k > P_1; \quad P_k < P_1 \text{ and } P_k = P_1$$

in accordance with which the process may go in the direction of reduced or increased pore volume or stop altogether.

It follows from the equation given earlier that the expanding effect of the gas in a closed pore will be more important the greater the initial radius of the pore. In the process of heating a porous solid, pores of relatively large initial diameter may even grow as a result of gas pressure (if, of course, the gas does not diffuse from the pores into zones of lower pressure or if its diffusion has

no substantial effect on the over-all picture).

It was stated above that a vacancy-concentration difference re-
sults in an increased rate of overgrowth of fine pores as compared
with the large pores, and that the small pores may become smaller
at the expense of an increase in large-pore volume. This phenomenon
acts in the direction of more intensive gas-pressure increase in the
fine pores as compared with the large ones. The retarding effect of
this factor on the process of pore-volume reduction will obviously
be more strongly manifested for fine pores.

Thus, when closed pores of various diameters are present in the
solid, their overgrowth will be nonuniform and will depend on many
factors, some of them acting in opposite directions and having non-
uniform effects on various pores and in various stages of the sinter-
ing process.

The process in which the volume of pores that communicate with
one another and with the surface of the solid (which is the case up
to a certain point in time in sintering of loose-poured powders) is
reduced obviously takes place without the above complicating phenomena.
In this case, given a constant value of the diffusion coefficient,
the rate of the body's volume change is constant in time, and its
order of magnitude and the duration of the sintering process may be
determined accordingly from Eqs. (48) and (53).

Experimental data on the kinetics of sintering at constant tem-
perature (Fig. 27) indicate that in actuality, the shrinkage of the
solid during this process is proportional to the square root of time.
As was shown by Pines [83], this is the result of a change in the
self-diffusion coefficient in consequence of the above "relaxation"
(distortion-relief) process, which takes place simultaneously with
sintering.

- 100 -

As we know, like many other properties of crystalline solids, the self-diffusion coefficient depends on the degree to which their crystal lattices are distorted (Chapter 1, §3). It is therefore natural that any change, and in particular any reduction or relief of such distortions in the process of heating the body will affect its rate of sintering. It should only be remembered that in the "relaxation" process, the crystal lattice approaches an equilibrium state, but nevertheless normally does not reach it in practice.

τ, min
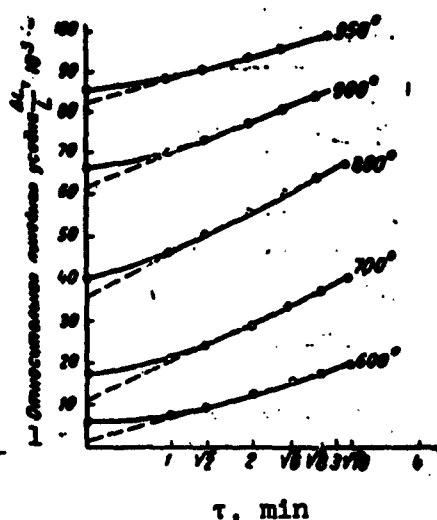
Fig. 27. Kinetics of isothermal sintering of pressformed copper powder with initial porosity of ~30% in specimen [83]. 1) Relative linear shrinkage $\Delta L_t/L \cdot 10^3$.

It has been established by research that the sintering rate of a crystalline solid having a lattice in a state far from equilibrium (a severely distorted lattice) is tens and hundreds of times (sometimes even several orders) higher than the sintering rate of crystals with only minor distortions. Thus, according to Kukolev and Dudavskiy [128], rapid sintering of a pressformed MgO powder produced by decomposition of $MgCO_3$ and having considerable distortion may be observed at a temperature of 600°, while MgO crystals without any essential crystal-lattice distortions sinter at noticeable rates only at temperatures of 1400-1500°.

The sintering rate depends on the perfection of the solid's crystal structure, the uniformity and extent of its particle-size refinement, the temperature of the process, the composition of the gaseous phase surrounding the grains, and the pressure of prior compacting (pressforming) of the powder.

- 101 -

A monodisperse (or nearly monodisperse) powder usually sinters more slowly than a polydisperse powder; this is accounted for by the shorter distance between grains and the larger surface area of mutual contact between them in the polydisperse powder (see §4, Chapter 1).

As the temperature is raised, the rate of the sintering process naturally increases in accordance with the increased mobility of the lattice structural elements and surface-tension forces.

The dependence of the rate of the process on the composition of the gaseous phase is known from the work of many authors [129-132] and others.* It has been established that a reducing hydrogen medium favors the sintering process of metallic copper, aluminum oxide (Fig. 28), and other powdered metals and oxides [129, 132], that beryllium powder sinters considerably more rapidly at a temperature of 1200° in an argon medium than in a medium of rarefied (residual pressure $5 \cdot 10^{-4}$ mm Hg) air [130], that a reduction of oxygen content in the gaseous phase accelerates the sintering process of certain oxides of variable valency [131], and so forth.
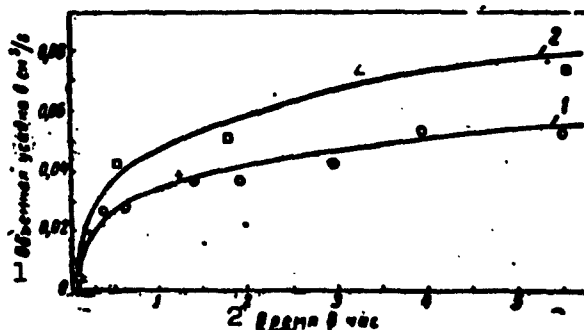
Fig. 28. Sintering of powdered α-alumina with an initial specimen porosity of ~0.3 cm³/g in media of air (1) and hydrogen (2) [132]. 1) Bulk shrinkage in cm³/g; 2) time in hours.

The mechanism by which the gaseous medium influences the sinter-

TABLE 13

Specific Gravity of Molybdenum Produced by Sintering for 3 hours

1	2	
	1000	1700
0	2.6	6.5
1000	4.6	9.1
2000	5.6	9.5
7000	7.6	10

1) Pressforming pressure in kg/cm^2; 2) specific gravity in g/cm^3 after sintering at the following temperatures in degrees.

ing process may be different in different cases. In general, this influence apparently reduces for the most part to effects on the composition and properties of the superficial grain layers and on the conditions of the diffusion that governs sintering.

A change in the composition of the gaseous phase (e.g., the oxygen content in it) may affect the number of vacant (in this example, oxygen) points in the lattice of the solid being heated; this will alter the conditions of its diffusion considerably and, consequently, those of sintering as well.

Another pattern of the effect under consideration is also possible. Suppose, for example, that a grain of the material to be sintered is covered with a film of substance B that has arisen on heating or was there at the outset, the composition of substance B differing from that of the grain material A. Then, depending on the differences between the properties of substances A and B and the properties of the gaseous phase, the latter may influence the sintering process in one direction or another. Thus, if the lattice of substance B possesses an energy higher than that of the lattice of substance A, a gaseous phase that contributes to elimination of B by, for example, its conversion into A, will favor the sintering process. In the contrary case

(when the elements of the substance-B lattice are more mobile than those of substance A), sintering will be promoted by a gaseous medium that promotes the formation of B. Other, more complex cases are also possible, for example, as a result of the system A+B having properties that differ essentially from those of either of its components.

Numerous investigations have established an essential intensification (in the majority of cases) of the powder-sintering process as a result of prior compacting of the powders.

Characteristic in this respect are the data of Grube and Schlecht [133] concerning the porosity attained in molybdenum on sintering in hydrogen after preliminary compacting of the molybdenum powder under various pressures (Table 13).

Under real conditions, the sintering process may be complicated considerably by its nonuniform progress at various distances from the surface of the solid, by an impurity content in the powder, or by other factors.

More rapid sintering takes place near the surface (here the vacancies diffuse through first). This is why we observe in masses of sufficiently large dimensions a thickening of the layer of sintered material from the surface toward the interior of the solid during the sintering process.

Depending on their properties and the temperature, impurities, and surface impurities in particular, may, in accordance with the above, change the diffusion rate to different degrees in the two directions; this will naturally affect the sintering rate in the solid phases. The formation of dense, solid films of impurities on the grain surfaces may retard this process.

The appearance of all types of lattice defects in the presence of impurities promotes the progress of sintering.

When reactions are effected in crystalline mixtures in industrial and research practice, we are frequently dealing with the type of liquid sintering noted above, which takes place in the presence and with the participation of a liquid phase.

This process, to which studies by Baykov [134], Belyankin [135], Budnikov [136], Berezhnoy [137], Kukolev [138-140] and many other investigators have been devoted, may include as important stages — in addition to the phenomenon described earlier, which are characteristic for "cold," "dry" sintering — phenomena in which the crystals dissolve in the liquid phase and the latter crystallizes.

Since solution and crystallization processes are diffusive, an understanding of the nature of and laws governing liquid sintering and judicious selection of the conditions for this process require analysis of the diffusive aspect of this process and consideration of its general qualitative laws.

As we know [46, 141-144], the solubilities of solid particles of different sizes are different. Large crystals placed in a liquid phase may grow as a result of solution of finer crystals in them [141, 145]; this results in a decrease in the system's thermodynamic potential. This decrease is particularly marked in cases where the fine crystals or crystalline aggregates are produced by grinding and, as a result, contain more of the various types of defects than large crystals. Such a recrystallization phenomenon may be of great importance in the process of liquid sintering. This effect may have as its result growth of large crystals or their being overgrown by small crystals — processes that are frequently unjustifiedly regarded as simple sintering of the "cold" type with a wetting or "cementing" effect of the liquid phase. Sintering in the presence of a liquid phase naturally depends on the latter's properties (which are primarily deter-

- 105 -

mined by its structure) and relative quantity.

The investigations of Berezhnoy [137] and Kukolev [138-140, 146, 147] showed a dependence of the rate of the liquid-sintering process on the viscosity and wetting ability of the melt: other conditions the same, the process will proceed more rapidly the lower the viscosity and the greater the wetting ability of the liquid phase.

In a study of the sintering of alumina in various systems, Kukolev et al. [139, 146] arrived at the conclusion that the structure of the melt is of particularly great importance here: intensive crystallization and sintering take place, in accordance with the well-known argument of Danilov [148], under conditions in which the cibotaxic groups existing in the melt correspond to the short-range ordering of the crystallizing phase.

The phenomenon of liquid sintering still requires additional investigation. The influence of concentration (and supersaturation) of the liquid phase and the influence of the external pressure and other conditions of this process on its intensity should, among other things, be the subject of circumstantial study.*

* * *

Let us consider, as briefly as possible, the recrystallization process of solids. As we know, it consists in the formation of certain grains of the solid at the expense of others and takes place particularly rapidly in plastically deformed solids. Its external manifestation is a change in the sizes and number of the crystals. The nature of this process, which has a considerable influence on the properties of crystalline solids and reactions in mixtures of them, depends on conditions.

We distinguish between two forms or limiting cases of recrystallization: 1) recrystallization proper or primary or true recrystallization,

which is also known as work recrystallization, and 2) selective or secondary recrystallization.

The first of these forms develops from definite centers in plastically deformed solids. As it proceeds, new, differently oriented grains arise at the positions of the original grains.

The second form, on the other hand, has no relation to prior deformation of the solids, i.e., it may take place in solids with either deformed or undeformed lattices. In this case, the process reduces to coarsening of the grains by displacement of their boundaries, but not by grain coalescence, as is the case, for example, in sintering.

In plastically deformed solids, selective recrystallization most frequently takes place after mechanically-induced recrystallization. However, both of these phenomena may also proceed independently of one another and, in certain cases, simultaneously.

There exist various conceptions as to the motive force and physical nature of the recrystallization processes.

A reduction of the solid's thermodynamic potential as a result of either a reduction of the total boundary area between grains or relief of distortions and stresses in the lattices or both of these effects simultaneously should be regarded as their motive force. The relative importances of these effects in different cases and in different stages of the given process may not be the same.

It would be useful to evaluate the magnitude of the energy change in the processes under consideration. According to experimental data [149], ~0.5 to 1 kal/g is liberated in annealing of a deformed metal; for copper, this comes to 30 kal/g-atom. This energy is liberated partly during recovery and partly during recrystallization. Grain growth is accompanied by a relatively small (in order of magnitude) heat effect. Assuming that the grains represent close-packed cubes, Sirs

[150] found that the surface energy of the grain boundaries is $\sim 10^{-5}$ kal/cm^2.

This signifies that the surface energy at the boundaries of 10^{-3}-cm copper grains is ~ 0.21 kal/g-atom. When the grain size is increased by a factor of 10, about 0.19 kal/g-atom is released. It is interesting to compare this quantity with the heat of fusion of copper, which is 3100 kal/g-atom.

In the majority of cases, work recrystallization is effected in a deformed material by formation and subsequent growth of seeds of unstressed material. This growth of grains with undistorted lattices takes place as a result of migration of particles of the solid (atoms, etc.) from distorted to undistorted crystals. Thus, as a result of work recrystallization, we obtain crystals or, more precisely, granules that are more or less free of distortions and, in any event, more stable than the initial crystals.

In accordance with the mechanism of this process, which has much in common with phase transformations, its kinetics may be described by the use of the quantities $\underline{n}$ and $\underline{c}$, which characterize the rate of formation of the centers and the linear growth rate of the new crystals. The values of these quantities depend, as has been shown by numerous investigations [46, 151-157], primarily on the purity of the solid, the degree of its deformation, and its grain size, as well as on the temperature of the process.

It has been established that pure substances recrystallize at a particularly rapid rate. Small quantities of impurities (sometimes < 0.01%) may lower the recrystallization rate by several orders, so that the so-called recrystallization temperature is increased by hundreds of degrees [46, 151-153].

The influence of dissolved impurities is particularly important.

By changing the forces and energy of interatomic interaction in the solid, soluble impurities simultaneously affect the activation energy of the diffusion effects and, consequently, the recrystallization process. Here, an impurity that increases the energy of interatomic interaction (as is the case in the overwhelming majority of cases) naturally reduces the mobility of the atoms and retards diffusion and recrystallization [153].

Preliminary deformation of a solid (an increase in its degree of deformation) influences the values of c and n (the latter in particular) in the majority of cases to accelerate recrystallization.

In a polydisperse solid, the large grains, which possess a lower surface energy, grow with particular rapidity in primary recrystallization.

Both the rate of seeding and the rate of crystal growth are extremely sensitive functions of temperature. At a certain degree of deformation of the solid, the dependence of growth rate on temperature may be expressed approximately by the formula

$$c = c_0 e^{-\frac{Q_c}{RT}},$$

where Q_c is the activation energy for crystal growth.

The value of n varies as a function of temperature in the same manner; here, we know that $Q_n \approx Q_c$; only for small deformations ($< 5\%$) is $Q_n > Q_c$.

Finally, it has been established that at constant temperature, the seeding rate n of the crystal centers increases considerably as the process advances, while the average growth rate c shows virtually no variation in time in the majority of cases [154-157].

We frequently speak of the recrystallization or initial-recrystallization temperature that is characteristic for a given substance.

These terms refer to the temperature at which the process under consideration attains an appreciable rate (i.e., an abrupt, stepwise rise in this rate), which, as will be clear from the above, depends on many factors, including the degree of deformation of the material being heated. As the latter increases, the recrystallization temperature drops.

According to Bochvar, the amplitude of vibration necessary to effect the process of recrystallization is, as in the case of fusion (pages 116, 117), a certain fraction of the crystal-lattice constant (a smaller fraction for crystallization, naturally, than for fusion). Proceeding from this, Bochvar [158, 159] arrived at the conclusion that if we disregard complicating factors, the recrystallization temperatures of the various metals should constitute the same fraction of their melting points. Actually, as Bochvar established on the basis of experimental data and as has been confirmed by Limpt [160] by theoretical calculation, $T_{rekr} \cong (0.35 \text{ to } 0.40)T_{pl}$.

The conditions and mechanism of seed formation may vary. Since the motive force of this process is the difference between the system's thermodynamic potentials, we may readily imagine that the preferential points of seed formation should be points at which "order and disorder" arise, i.e., microvolumes with undistorted crystal lattice in a mass possessing a defect structure. Obviously, the motive force of the seeding process will be the higher the greater the difference in the degrees of ordering in the solid's lattice and, consequently, the greater the nonuniformity with which stresses are distributed in its volume.

Naturally, the rate of the process must depend here on the distance between points having different degrees of ordering. Consequently, it will be helpful to introduce the concept of a conventional

- 110 -

distortion gradient in order to characterize the motive force of the process and to understand certain of the qualitative laws governing it:

$$\nabla H = \frac{H_1 - H_2}{L_{1-2}},$$

where H_1 and H_2 are the respective degrees of disturbance of the lattice in the first and second compared points of the solid and L_{1-2} is the distance between them.

To a certain degree, this gradient is analogous to the temperature and concentration gradients with which we work in the theory of heat- and mass transfer.

Making use of such a gradient, we may write that the intensity i of the seeding process at the given temperature must be in first approximation proportional to ∇H and to the number n of disturbances per unit volume of the solid:

$$i = -K \nabla H n, \tag{55}$$

where the minus sign indicates that the process is going in the direction of reduced distortion.

Experimental evaluation of the true or average value of the distortion gradient would probably make it possible in many practical cases to account quantitatively for the intensity of recrystallization seeding in the regions (more precisely, near the regions) of large lattice distortions.

The mechanisms of the seeding and growth processes of crystals are apparently highly similar. Certain authors even assume that seeding is essentially growth of centers that already exist (subgrains) in the solid. However, energy comparisons of these processes indicate that in actuality, the activation energy of seeding (the process involved in the emergence of a new surface) at relatively low

deformations is greater than the activation energy of grain growth.

At any given temperature, the seed growth rate is higher than the formation rate. As the degree of deformation rises, the rate of formation increases more rapidly than the growth rate. As a result, the average grain size is smaller toward the end of primary recrystallization the higher the degree of deformation.

The number of disturbances per unit volume of a solid, the value of the average differential (or gradient) of the disturbances, and the degrees of their nonuniformity, which affect the kinetics of recrystallization (chiefly the seeding rate) depend on the size of the original grains: the smaller the grain size, the larger will be their number and the steeper will be the distortion gradient (the distortions being particularly marked at the grain boundaries) and, consequently, the larger will be the number of seeding centers for a given temperature.

Since regions with increasingly low degrees of distortion become seeding centers as the temperature rises, the result will be an increase in the number of zones that may act as seeding centers. Consequently, the relatively quick recrystallization that occurs at higher temperatures results in the formation of smaller grains.

The use of these and certain other points makes it possible to regulate the grain size of the solid that results from recrystallization.

The motive force of the secondary (selective)-recrystallization process is the surface tension of the grain boundaries, so that the process advances in either the presence or absence of prior deformation. The action of surface-tension forces is what accounts for [83, 125] the direction of the previously mentioned displacement of the boundaries between the grains in the secondary-recrystallization process:

the boundary moves from a crystal that is under tension by the forces of interphase surface tension toward an adjacent crystal that is compressed by the same forces (normally, large crystals "eat up" smaller sized crystals). This results in a reduction of the system's internal surface energy.

The kinetics of the process described here is similar as regards its basic features to that of primary crystallization. However, the rate of secondary recrystallization increases with diminishing size of the original grains. Here, the growth rate is considerably lower than in primary recrystallization.

Using theoretical analysis as a basis for comparing the possible rates of recrystallization and sintering for a given order of grain and pore sizes, Pines [83] arrived at the conclusion that the first of these processes must take place considerably more rapidly than the second, so that in practice, recrystallization precedes sintering in polycrystalline solids with distorted lattices, i.e., sintering takes place in a recrystallized solid.

However, this proposition requires further detailed experimental investigation.

§3. FUSION. HETEROGENEOUS EQUILIBRIUM

Understanding of the essential nature of and laws governing the fusion process naturally requires a conception of the similarities and dissimilarities in the structure and properties of solids and liquids.

Until comparatively recently, it was believed that the structure of fluids lacks any form of regularity even at temperatures close to the crystallization temperatures, i.e., that in the sense of the arrangement of its particles (atoms, ions, molecules), liquids are as amorphous as gases.

This conception, which was reinforced by the close association between the liquid and gaseous states as established by the van der Waals theory, was essentially an idealization of the liquids, and one which approximated reality only at very high (near-critical) temperatures and large volumes. In actuality, the so-called "long-range order" in the arrangement of the molecules or atoms of a liquid is lacking, in contrast to the situation in crystals. However, there is a "short-range order," i.e., a regularity in their arrangement in the immediate vicinity of any given atom (or molecule), which drops off rapidly with increasing distance. At not particularly high temperatures, the liquid is crystal-like in structure and reminiscent of a microcrystalline solid. The regularity in the structure of liquids, or their degree of crystal-similitude, increases as we approach the crystallization temperature and differs only slightly from the regularity of the solid's structure near this temperature.

This is confirmed by the results of many investigations. It is known that formation of crystallization centers, takes place in supercooled liquids. These crystallization centers, which are particularly distinct in complex liquids with extremely large molecules, are obviously submicroscopic crystals.
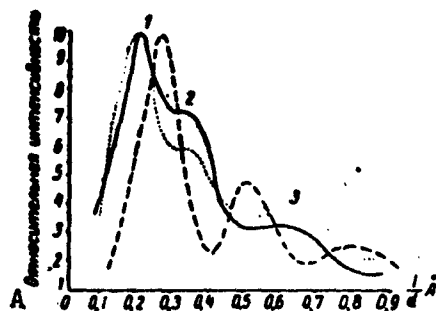
Fig. 29. Variation of intensity distribution in water as a function of scattering angle (results of x-ray investigation of water). 1) First maximum at 3.27 A; 2) second maximum at 2.27 A; 3) third maximum at 1.45 A. A) Relative intensity.

Further, it has been possible as a result of x-ray and electron-diffraction examination of many liquids, including water, mercury, and fused silicates, to establish that their structure is nearly crystalline [161-163].

X-ray diffraction patterns of liquid mercury indicate that the first few layers of atoms surrounding any arbitrarily selected atom are arrayed about it preferentially at the same distances as in the single crystal. Thus, the "short-range ordering" is basically retained in the arrangement of the atoms. Here we observe a certain scattering of the atoms about the positions that might be expected in the case of an ideal crystalline structure for mercury. The value of the average displacement of the atoms (with respect to their ideal positions) increases in proportion to the square root of distance, so that there is no "long-range ordering" in the structure of liquid mercury.

Let us note that the quasi-crystalline structure of a liquid sometimes differs from the crystalline structure of the same substance. Thus, in the solid state, mercury crystallizes in the form of a rhombohedral lattice, while in the liquid state it makes an approach to a close-packed hexagonal lattice; ice has a crystal structure similar to that of tridymite, while water resembles quartz in this respect.

The distinction between the structure of water and that of ice has been exactly established by x-ray investigation (see Fig. 29, which has been borrowed from the work of Bernal and Fauler [164]), and has been confirmed by comparison of their physical properties (e.g., density) and energy calculations [45].

The temperature of a liquid naturally affects the rate and nature of the vibrations of its particles. As the temperature rises, we may observe a series of transitions in the thermal-agitation pattern of the liquid particles from vibrations about the virtually unchanging (or very seldom changing) equilibrium positions characteristic for the solid to the exceedingly intense translational motion of particles that is characteristic for a gas and disturbed only collisions between

- 115 -

them.

To form a judgement as to the nature of thermal agitation in liquids, it is interesting to compare their heat capacities with those of the corresponding solids. It is known that the heat capacity of liquids, particularly such simple liquids as fused metals, are always higher than the heat capacities of the corresponding solids near their crystallization temperatures. Thus, the heat capacities of mercury, tin, and lead in pure form are 4, 13, and 28% higher, respectively, than in the solid form. This heat-capacity increase corresponds to the energy of amorphization of the solid, which begins on fusion; amorphization of a solid is frequently detected in the form of its latent heat of fusion.

The heat capacities of many simple solids such as metals and the inert elements undergo virtually no change on fusion, remaining very close to 6 kal/g-atom, i.e., to a value corresponding to Dulong and Petit's law. We obtain this value if we use as our point of departure a conception of the oscillatory motion of the atoms about certain mean equilibrium positions. The absence of any essential difference between the heat capacities of a given substance in the solid and liquid states suggests that the nature of particle thermal agitation undergoes no essential change on fusion: at temperatures close to the melting point, this motion reduces to oscillation of the particles about certain equilibrium positions.

Proceeding from these concepts, which were developed chiefly by Frenkel' [44, 45], we must conclude that fusion is not a transition of the substance from the crystalline state into an amorphous state, but simply partial amorphization of the solid resulting from disturbances to "long-range ordering" with retention of "short-range order" in its structure. In many respects, fusion is analogous to transition

of the substance into another modification.

To bring a solid into the liquid state, i.e., for the above partial amorphization to take place, it is, of course, necessary to expend energy to overcome the forces operating between the elements of its lattice: fusion intervenes when the average energy of lattice-element vibration is sufficiently large to achieve a certain disturbance of the bonds between them. According to Lindeman [165], the linear oscillation amplitude a_{pl} of the atoms of the solid at which they are torn from the crystal lattice in the fusion process constitutes a certain fraction of the average interatomic distance δ:

$$a_{ui} = \frac{\delta}{m},$$

where $1/m$ is a fraction of the average interatomic distance that depends on the structure of the solid and is determined experimentally. It is therefore natural that the solid's heat of fusion Q should depend on the composition, structure, shape, and relative positions of the structural units in the crystals, which are built from atoms, ions, or molecules. The value of Q in cal/mole varies over a wide range for various classes of substances — metals and inorganic and organic compounds — as has been shown by experiment.

The melting point of a crystalline solid must depend on its lattice energy, which is determined by its basic parameters (see pages 19-22). As we know, each solid has a certain exactly reproducible (at a given pressure) melting point,* at which many of its properties change abruptly. We are speaking, of course, of structure-sensitive properties — properties that depend essentially on the retention or disruption of "long-range order" in the structure of the solid. Here, structure-insensitive properties, which depend only on "short-range order" in the solid's structure, undergo no essential changes, in much the same

way as occurs on transition from a single crystal to a microcrystal-
line aggregate.

The melting point of a solid must, in general, depend on external
conditions, and in particular on pressure. In accordance with the
laws of thermodynamics, a pressure increase gives rise to an increase
in the material's melting point, if (as is usually the case) fusion
of the substance is accompanied by an increase in its volume.

A drop in pressure leads to the converse result and, by applying
a sufficiently large "negative pressure" to a solid from all sides,
it will be possible to "melt" it, i.e., bring it into the liquid (quasi-
crystalline) state at any temperature from absolute zero to the melt-
ing point of this solid at atmospheric pressure. Theoretically, such
fusion is quite possible.

In actuality, the melting points of substances depend only very
insignificantly on pressure. It is known, for example, that a 130-atm
change in the pressure over ice changes its melting point by only
1°.

For this reason, and particularly because reactions in solid
mixtures are usually conducted under atmospheric pressure (or a pres-
sure close to atmospheric), we may disregard the change in melting
point of the mixture components as a function of pressure in the over-
whelming majority of the cases that are of practical interest to us.

However, this change must be taken into consideration in cases
where the reaction is conducted under a pressure that differs con-
siderably from atmospheric (as was the case, for example, in certain
experiments of Spring [166]).

. # # #

To investigate the conditions under which reactions proceed be-
tween solid substances and to account for their behavior under these

conditions, it is first of all necessary to have available information concerning the various heterogeneous equilibria that prevail at high temperatures. Physicochemical analysis of the corresponding equilibrium systems is therefore a necessary element in analysis of any nonsteady process in a solid mixture.

We can distinguish three interrelated important trends in physico-chemical-analytical investigation:

topology, or qualitative study of the general geometrical properties of the diagram of state (Gibbs, Rozebom, Kurnakov and his school);

metrics, i.e., quantitative study of the relationships between the quantities characterizing the processes that take place in the system and the elements of the diagram of state (Stepanov, Storonkin);

study of the cause for the relationship between the topological and metric characteristics of the equilibrium diagram on the one hand with the structure and properties of the system components on the other (Pines, Danilov, Kamenetskaya, Kravchenko, and others).

Recently, a topoanalytical method for study of equilibrium systems has been developed in the work of Palatnik and other authors and successfully applied; this combined the geometrical and analytical methods of investigation.

Let us first pause to discuss topology. As we know, the phase-rule-governed relationship between the number of phases and the number of components in the system may vary with changes in the prevailing external conditions. The conditions under which a state change occurs in the system are related to the phase composition. For a given set of external conditions, the phase composition will depend on the thermo-dynamic properties of the components. The most specific and convenient form for expressing these interrelationships consists in

graphic characterization of the heterogeneous equilibrium by means of concentration-temperature diagrams, the so-called diagrams of state. The [Soviet] [167-170 and others] and foreign [171, 172 and others] literatures contain extensive collections of these diagrams.

Assuming that the reader is familiar both with the principle on which such diagrams are constructed from experimental data and, specifically, from solution (melt)-cooling curves, and with the reasons for the differences between the most important forms of these diagrams (Fig. 30), we recall that the plane of the diagram of the system A-B e.g., that shown in Fig. 30a, is divided by the curves of the initial-crystallization temperatures $T_A E$ and $T_B E$ and the horizontal eutectic line FG into four regions.
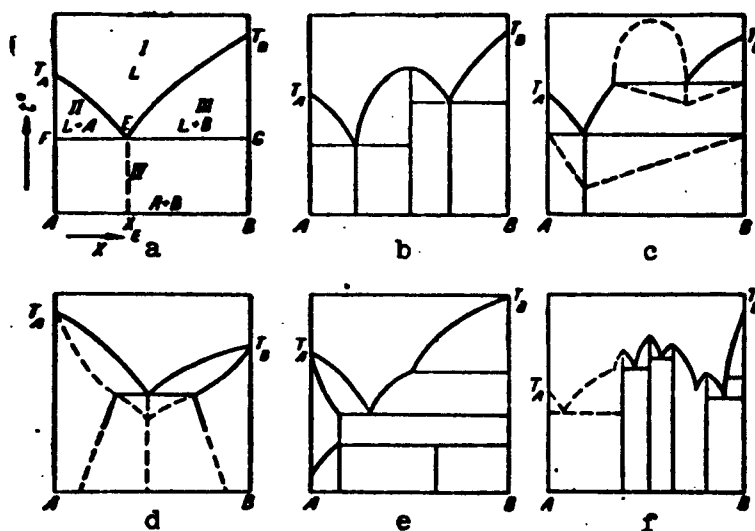
Fig. 30. Basic forms of diagrams of state for two-component systems. a) Simple eutectic (full solubility in liquid phase and absence of solubility in solid phases); b) chemical compound; c) limited solubility in liquid form; d) limited solubility in solid form; e) polymorphic transformations; f) several chemical compounds.

Within the limits of region I, which is bounded below by the liquidus curves, there is only a single liquid phase, the composition of which varies from A to B. Between the liquidus curves and the

eutectic horizontal we have two two-phased regions II and III, within which a variable-composition liquid phase is in equilibrium with a single solid phase of constant composition: A in region II and B in region III. Finally, below the eutectic horizontal we have region IV, in which two solid phases of constant composition — crystals of A and B — coexist.

According to the phase rule, the liquids of region I have two degrees of freedom, while the liquid-solid systems of regions II and III have one degree of freedom, as do the solid systems of region IV. Like the possibility and direction of spontaneous advance of any processes in the system, its equilibrium conditions are governed by general thermodynamic relationships.

If a certain system exists in two states simultaneously at a given temperature and pressure, e.g., in the crystalline and liquid states, in the form of a solution and a mechanical mixture, and so forth, then that one of its states in which the thermodynamic potential of the system is lower will be the stable one. Thus, crystals of any substance possess higher thermodynamic potentials at temperatures above its melting point than does a melt of this substance, so that they are unstable. Thus, if the thermodynamic potential of a system in the form of a solution is larger than the energy in the mechanical-mixture form, the solution will be less stable than the mixture, and it will go spontaneously into the mixture state. In the contrary case, the reverse transformation will also take place spontaneously.

The thermodynamic potential of a mixture of components at the same temperature and pressure is an additive quantity. It depends on the mass of the materials forming the system.

The specific thermodynamic potential of the system (that referred to 1 g or to 1 mole of the material), consisting of any phases is a

linear function of the weight (or mole) fractions of the components and may be computed by the displacement rule

$$z = z_A X_A + z_B X_B + \ldots + z_n X_n,$$

where z_A, z_B, ..., z_n are the specific thermodynamic potentials of the mixture components and X_A, X_B, ..., X_n are their weight (or mole) fractions in the mixture.

Obviously, the specific thermodynamic potential of a nonuniform binary mixture will be expressed by a straight line, and that of a uniform binary mixture (solid or liquid solution, gaseous mixture of two components) by a curve. Here, according to what we said above, the thermodynamic-potential curve of a stable uniform mixture such as a solution will lie below the corresponding straight line computed by the additive rule over its entire length.

As was shown as long ago as 1899 by Rozebom [173], we may obtain the shape and establish the type of diagram of state for a heterogeneous system by applying the phase rule and the thermodynamic-potential curves. The principle of such reasoning reduces to examination of a series of isotherms of the system's specific thermodynamic potentials, establishment of the phases in equilibrium at each selected temperature, and construction of a diagram showing the phase-transition temperatures as functions of the system's composition.

It will be easiest to reproduce the sequence followed in this reasoning by reference to the example in which the diagram of state of a binary system characterized by full solubility in the liquid state and zero solubility in the solid state, i.e., a diagram with a simple eutectic, is derived.

The isothermal curves of specific thermodynamic potential are shown at the top in Fig. 31 for such a system at six different temperatures, while the bottom of the figure shows the diagram of state
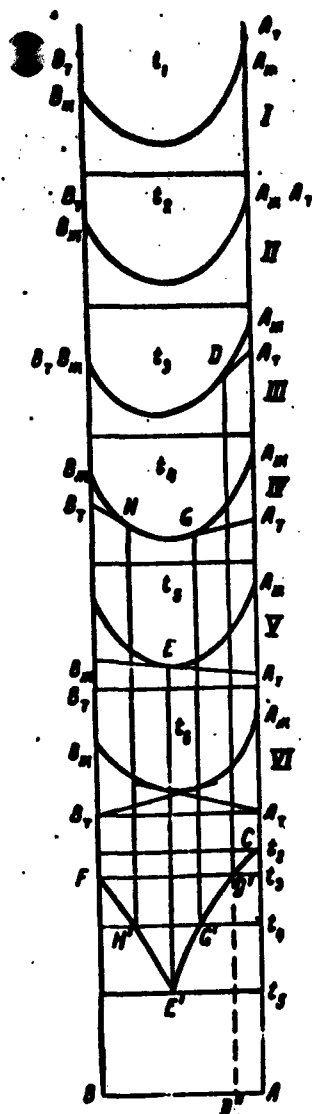
Fig. 31. Iso-
thermic curves
of specific
thermodynamic
potential of
system with
simple eutectic.
X = liquid;
T = solid.

obtained for the system from these curves.

The points A_t, B_t, A_{zh} and B_{zh} express the
values of the specific thermodynamic potentials
of the components A and B of the system,
in the solid and liquid states, respectively.

At a temperature t_1 in excess of the melting
point of the higher-melting component A, the
points A_t and B_t are naturally situated higher
than the points A_{zh} and B_{zh} (diagram I).

As the temperature is lowered, the point A_t
approaches the point A_{zh}, and point B_t approaches
B_{zh}. When the system's temperature t_2 is equal to
the melting point of component A (diagram II),
the points A_t and A_{zh} coincide; then the point
B_t is above point B_{zh}, since component B has
melted.

On further depression of the temperature,
point A_t lies below A_{zh}. In this case, we may
draw from point A_t a tangent to the curve of
specific thermodynamic potential, indicating
equilibrium of the solid component A with a cer-
tain solution whose composition is given by the
point of tangency.

If the temperature t_3 is equal to the melting
point of component B, points B_t and B_{zh} will coin-
cide (diagram III). Let us pass a tangent to the
curve from A_t and a vertical line through the point
of tangency D.

Noting the temperature t_3 on the diagram of state, we draw the

isothermal line FD' corresponding to it; the point D' of intersection of this line with the above vertical line indicates the temperature at which crystallization begins in a system of the composition characterized by point D". We also mark the melting points C and F of the components A and B on the diagram. When the system has been cooled to the temperature t_4, which is lower than the melting point of B (diagram IV), the points A_t and B_t will lie below the temperature t_3. Let us pass tangents to the curve from these points. The points of tangency G and H give the compositions of solutions that are in equilibrium at the temperature t_4 with the respective solid components A and B. As before, we use diagram IV to obtain points G' and H' on the diagram of state.

A further decrease in the system's temperature is accompanied by a shift of points G and H toward one another and, finally, the two tangents merge into a single straight line at the eutectic temperature t_5 (diagram V); here, both solid components are in equilibrium with the same solution, the composition of which is expressed by point E. Transferring this point to the diagram of state gives the eutectic E'.

Cooling of the system to temperatures below t_5 results in diagram VI. Here, mechanical mixtures of the solid components A and B are in steady-state equilibrium: the specific thermodynamic potential of such mixtures is lower than that of mixtures of solid A and B with the solutions in equilibrium with them (the latter equilibria are unstable under the given conditions).

Connecting the points obtained in this way on the diagram of state, we obtain the curves FH'E' and CD'G'E' for the initial-recrystallization temperatures, which correspond to separation of the respective components B and A into the solid phase.

Condensed-state diagrams of other types of systems can be derived

in the same way. Here, just as in the construction of the diagram of state from the cooling-heating curve, each point is constructed from experimental data.

Until comparatively recently, this principle was the only one for constructing diagrams of state. Only certain general thermodynamic premises were drawn upon in constructing them, as was done above.

However, an equilibrium diagram can be constructed by thermodynamic methods exclusively and analytical expressions obtained for the curves. (or surfaces) separating the existence regions of mixtures of the different phases, as well as the curves expressing the mutual solubility of the system components. The form of these analytical expressions and the shape of the curves (or surfaces) corresponding to them are determined by the potential energy of the system, which depends on physical factors. Here, the diagrams of real systems usually differ essentially from those of ideal systems; this is consistent with the differences in the properties of different systems.

The idealness criteria are different for different types of phase equilibrium, e.g., for eutectic-type systems and systems with continuous solid solutions [174, 175].

A liquid solution is said to be ideal when reciprocal substitution of molecules of the components forming it does not affect the molecular force field. An important conclusion expressed for the first time in 1890 by Schroeder, the founder of the theory of ideal solutions [176], proceeds from this property: "When a solution is subject to Raoul's law in a definite temperature region, the heat of solution of the solid is equal to its heat of fusion."

Taking the temperature interval between the melting points of the components and the eutectic point of the system as the boundaries

of the "definite temperature region," we may extend Schroeder's proposition to the entire field of phase equilibria between liquids (melts) and crystals in the condensed system.

According to Schroeder's equation [176], the molar concentration x (of saturation) of the component in the solution of such an ideal system at a temperature T_1 depends only on the melting point T and molar heat of fusion Q of this component:

$$\ln x = \frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right).$$ (56)

where R is the gas constant and T and T_1 are absolute temperatures.

Obviously, the shape of the T:ln x or T:x curves described by this equation is determined by the value of the fusion entropy of the component in question, $S = Q/T$.

Given identical melting points of the components, the eutectic temperature will be lower, and the descent of the liquidus curves will be steeper the smaller the entropy (it will be recalled that the average fusion-entropy values of the majority of elements S = 2-3, those for inorganic compounds S = 5-7, and those for organic compounds S = 9-12).

Solving equations of type (56) simultaneously, Kravchenko [177] proposed the following equation for computing the composition of the two-component eutectic mixture of an ideal system:

$$x_1 + a x_1^K - 1 = 0,$$ (57)

where $K = \frac{Q_2}{Q_1}$, $a = 10^{\frac{-Q_2(T_1 - T_2)}{4.57 T_1 T_2}}$. the values of x, Q, and T are the same as in Eq. (56), and the subscripts 1 and 2 denote quantities referring to the first and second components, respectively.

Many qualitative laws of ideal condensed systems, and Eqs. (56), (57) in particular, are found to be invalid for real systems in the overwhelming majority of cases. Knowledge of such relationships is,

however, as correctly noted by Kravchenko [175], also necessary for practical purposes, just as knowledge of the ideal gas laws is necessary in dealing with real gases. In real systems, intermolecular forces are in operation, and these determine the shape of the curves (or surfaces) of the diagrams of state.

Numerous attempts to compute diagrams of state to take the action of these forces into account have been reported. One of the many forms of equilibrium was examined by Becker. Becker [178, 179] showed that the decay curve of a binary solid solution may, when the decay takes place without lattice modifications (lattices of both components identical), be expressed by the equation

$$\frac{kT}{zU} = \frac{1-2x}{\ln\frac{1-x}{x}},$$

(58)

where z is the coordination number, x is the concentration, and U is the so-called displacement energy (see below).

In being the first to adopt a consistent standpoint in theoretical investigation of the various phase transformations that take place with heat effects, Pines [180, 181] demonstrated the dependence of the diagrams of state on the nature of the intermolecular bonds and derived approximate equations for the equilibrium curves of a number of simple binary systems. Here, like Becker, Pines did not take into account the dependence of bonding energy on concentration, and assumed that the solutions mix without undergoing changes in volume. The conditions formulated by Pines do not exhaust all possible cases in which various diagrams of state originate. Moreover, in his analysis of the eutectic and peritectic diagrams of state, Pines identified the triple point with the critical point in decay (stratification) of the solid solution.

Subsequently, a more extensive and rigorous investigation of the

influence of intermolecular interaction between the components on phase equilibrium in binary system was carried out in the work of Danilov and Kamenetskaya [182-184].

Recently, as a result of the studies of the above investigators and those of Livshits, Stepanov, Storonkin, Finkel'shteyn, and other authors, it has become possible in many cases to make rather accurate quantitative calculations of the diagrams of state of real systems.

The type of the diagram of state and its characteristic are determined in general by the magnitude of the bonding energies between like and unlike molecules in the coexisting phases of the system. This energy may be regarded as the work required to break the bonds between the corresponding molecules, taken with the minus sign.*

Let U_{AA}, U_{BB}, and U_{AB} express the respective bonding energies between the different molecule pairs formed by components A and B. Then the total bonding energy will be equal to the sum of the bonding energies of all molecular pairs of the types AA, BB, and AB formed by the components:

$$E = N \left[x(1-x)U + (1-x)U_A + xU_a \right], \qquad (59)$$

where N is the total number of molecules in the mixture, $\underline{x}$ is the fraction of component-A molecules, U_A and U are the energies attributable to one molecule of the corresponding component and U is the displacement energy, which represents the diff rence between the bonding energies of like and unlike molecules (or, in the case of simple substances, atoms): $U = U_{AB} - (U_{AA} + U_{BB})/2$.

It is obvious that $U = 0$ when the bonding energy between unlike molecules is equal to the arithmetic-mean bonding energy between like molecules (or atoms); $U > 0$ when the bond between like molecules is stronger than that between unlike molecules and $U < 0$ when the bond

between unlike molecules is stronger than that between like molecules.

If we characterize the tendency of unlike molecules or atoms to combine in this manner (the smaller U, the stronger will be this tendency), the value of U is extremely important in determining the nature of the diagram of state.

Let U' and U'' be the "displacement energies" in the solid and liquid phases, respectively.

If in the temperature interval under consideration, the pure components do not undergo any transformations and $U' = U'' > 0$, i.e., if like molecules are bonded more strongly than unlike molecules, the solid solution decays.

If $U' = U'' = 0$, i.e., if the bonds between like and unlike molecules (atoms) are the same in both phases and a phase transformation accompanied by a heat effect (e.g., fusion) takes place in the pure components, we obtain a "cigar-type" diagram for the solid solution (see Fig. 30).

If $U' \neq U''$ and a phase transformation takes place in the temperature range under consideration, but there is no stratification or decay, the equilibrium curves have a common point (maximum or minimum). Here, in cases where $U' > U''$, i.e., when the tendency of unlike atoms to combine is more distinct in the solid solution than in the liquid solution, we obtain a diagram with a maximum, while a minimum appears in the contrary case.

If $U' = U''$ and $T_A = T_B$, crystallization takes place at constant temperature.

Suppose there is no solubility in the solid phase. This occurs at very large values of the displacement energy U'' in the second (solid) phase. This gives the following equation for the left part of the liquidus for $y = 0$ (pure component A in the solid phase):

$$x^2 U' + kq_A(T_A - T) + kT \ln(1 - x) = 0 \qquad (60)$$

and for y = 1 (pure component B in the solid phase), the following equation for the right part of the liquidus:

$$(1 - x^2)U' + kq_B(T_B - T) + kT \ln x = 0, \qquad (61)$$

where $\underline{k}$ is Boltzmann's constant and q_A and q_B are the differences between the entropies of phases I and II at the phase-transition point for the corresponding components, referred to one molecule (atom) of the mixture:

$$q_A = \frac{S_A' - S_A''}{N}. \qquad (62)$$

The right and left parts of the curve intersect at the eutectic point, the coordinates of which are x_e and T_e. At U' = 0, these equations become Schroeder's equations for "ideal" solutions:

$$\ln(1 - x) = \frac{Q_A}{R}\left(\frac{1}{T_A} - \frac{1}{T}\right) \qquad (63)$$

and

$$\ln x = \frac{Q_B}{R}\left(\frac{1}{T_B} - \frac{1}{T}\right). \qquad (64)$$

where $Q_A = Rq_A T_A$ and $Q_B = Rq_B T_B$ are the heats of fusion of the corresponding components.

Fig. 32. Relative positions of solubility curves for different values of "displacement energy."

Thus, the terms $x^2 U'$ and $(1 - x^2)U'$ of Eqs. (60) and (61) characterize the deviation of the solution from the ideal. Figure 32 gives a schematic representation of the influence of U' on the direction taken by the solubility curves: with U' > 0, the curve lies above that for U' = 0, while with U' < 0, its lies below it.

This means that if the bonding between like molecules (atoms) is stronger than that between unlike components, crystallization of the solid solvent begins earlier as the solution cools, i.e., at a higher

temperature (in reality, the bonding of unlike molecules is frequently stronger than that of like molecules).

Thus, the type of diagram of state is determined by the sign and relative magnitude of the displacement energies of the two phases, and, in some cases, by the relative amount by which the melting point of component A exceeds that of component B.

The above considerations and formulas, and the system of equations (60), (61) in particular, enable us to determine the concentrations of the coexisting (equilibrium) phases in the simplest binary systems for each temperature and thus to characterize their equilibrium diagrams with the aid of a few constants related to the intermolecular interaction (T_A, T_B, U', U", and $\underline{q}$) that have simple physical significance, some of which (T_A, T_B) are generally known, while others (U', U", and $\underline{q}$) are easy to determine.

If, for example, experimental values of x_e and T_e are known, it is easy to determine the value of the displacement energy U.

Further, knowing q_A and q_B, we may use Eqs. (60) and (61) to compute both branches of the liquidus curve.

Thus, determination of the phase-diagram curves reduces to finding a few constants. Experimental investigations naturally form the validity criteria for such calculations. Such investigations have been carried out by Danilov and Kamenetskaya, Pines, and Geguzin, and certain other authors.

Danilov and Kamenetskaya [182] obtained satisfactory agreement between the results of calculation and experiment for four binary systems possessing a eutectic point with total insolubility in the solid phases.

Pines and Geguzin [185] made a comparison of the calculated and experimental data for twenty binary systems with three different types

- 131 -

of equilibrium diagrams (1 — "cigar," 2 — with an equal-concentration point and 3 — with a eutectic point) and also obtained satisfactory agreement between the two types of data.

In another report [186], these same authors used the relationship found by Pines between the displacement energy and the heats of formation of the alloys and the heat capacity in the stratification region to determine the first-mentioned quantity. Investigation of five binary metallic systems produced satisfactory first-approximation agreement between the calculated data, which were constructed on the basis of thermal measurements, and the result of direct experimental determination of the equilibrium diagrams.

The possibility of approximate calculation of the diagrams does not, of course, make it possible to dispense completely with experimental determinations, but it may simplify the problem of the experimenter considerably and, in any event, make it possible to fix quantitative differences between diagrams of the same type and different types in simple form.

Determination of the displacement energies in different phases may be of interest in ascertaining changes in the nature of the atomic interaction in different systems on passage from the liquid phase into one of the solid phases or when certain atoms are replaced by others in the system. Information obtained in this way may, in general, be found useful for many purposes, and for development of a quantum-mechanical theory of alloys in particular.

In a number of cases, the results of the type of calculations described above may, however, depart from reality. Here we have in mind the fact that some of the studies described above (those of Pines) do not take into consideration the dependence of bonding energy on the distance between particles, which is a function of the concentration

- 132 -

of the solution, and assume that the solutions mix without undergoing any volume changes. Proceeding in general from the same approximation, the authors of other studies (Danilov and Kamenetskaya) take into account only the difference in the entropy jump that occurs on fusion of the components. In all of the studies cited, the internal energy of the system and its entropy are computed on the assumption of perfect mixing of the two species of atoms, i.e., assuming that the interaction between atoms exerts no influence on their positioning at the points of the crystal lattice. This corresponds to the approximation in the theory of regular solutions usually associated with the name of Hildebrand.

In reality, the residence of two atoms at ajacent points of the lattice does not represent two statistically independent events, as is the case in the approximation of regular-solution theory. As a result, the thermodynamic considerations and formulas set forth above are capable of providing an adequate description of the liquid solution's behavior only at moderately high displacement-energy values.

The experimental stratification curves of liquids come close to the theoretical in a region of temperatures that does not extend too far from the critical temperature. When the temperature is sharply depressed, the difference between the experimental and theoretical curves testifies to the inadequacy of the approximation described above.

Calculation of the free energy of a binary system in subsequent approximations taking into account the influence exerted by atomic interaction on the positions of the atoms in the crystal lattice is a matter that presents essential difficulties. Finkel'shteyn [187] recently showed that this influence is manifested in a decrease in entropy and internal system energy irrespective of the sign of the displacement energy; here, the free energy of the system (e.g., alloy) is reduced

- 133 -

in the final analysis. Livshits [188] succeeded at one point in ob-
taining an approximate expression for ΔF that was valid under certain
limited conditions. Using his derivations as a point of departure, we
may [187] obtain refined expressions for the so-called activity coef-
ficients, which enable us to characterize the thermodynamic behavior
of the system. However, exhaustive quantitative calculation of the
equilibrium diagrams by means of these coefficients is limited by the
fact that Livshits' reasoning is inapplicable in the low-temperature
region. This explains the importance of adequately precise experimental
determination of the activity coefficients for the system components.
Determination of these coefficients from vapor pressures measured with
tagged atoms offers great promise in this respect.
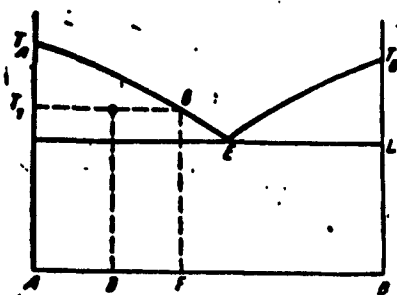
Fig. 33. Diagram of state of
two-component system with
simple eutectic (illustrating
lever rule).

Obviously, further development of
heterogeneous-equilibrium theory and,
in particular, elimination of the above
restrictions on its theoretical cal-
culation, combined with improvement
of methods for determining it experi-
mentally, should provide researchers
with a simple and highly effective tool
for the study of processes taking place
in mixtures of crystalline solids.

At the present time, equilibrium diagrams are being used to study
and compute crystallization processes, primarily the sequence in which
the crystalline phases are liberated and the changes in the properties
of the liquid phase on cooling and heating. Using such diagrams, it is
easy to ascertain not only the temperature at which the liquid phase
appears, but also the quantity of it at different temperatures; this
is highly important for analysis of processes taking place in mixtures

- 134 -

of crystalline solids.

The connecting-line and lever rules are used for this purpose.

As it applies to binary systems, the connecting-line rule runs as follows: if a system splits into two complexes at a certain temperature, the points corresponding to the composition of the system and those of these complexes should all lie on the same straight line.

According to the lever rule, the ratio of the quantities of the component complexes should then be equal to the reciprocal of the ratio between the lengths of the segments from the point corresponding to the system composition to the points corresponding to the component complexes. The lever rule proceeds from the following considerations (Fig. 33).

Suppose that at a temperature T_1 a system of general composition D consists of crystals of component A and a liquid phase of component F. If the amount of A crystals per unit weight of the system is $\underline{x}$, the weight of the remaining liquid phase at the temperature T_1 will be $1 - x$.

The quantity of component B in the system $1 \cdot AD$ is equal to the quantity of it in the residual liquid phase:

$$1 \cdot AD = (1 - x) AF, \tag{65}$$

from which

$$\frac{1}{x} = \frac{AF}{AF - AD} \tag{66}$$

and

$$(1 - x) = \frac{AD}{AF}. \tag{67}$$

Solving Eqs. (66) and (67) simultaneously, we obtain a mathematical formulation of the lever rule that expresses the ratio of the quantity of liquid phase to the quantity of crystals at the selected temperature T_1:

$$\frac{1 - x}{x} = \frac{AD}{DF}. \tag{68}$$

- 135 -

In Reference [189], which was devoted to a generalized "center-of-gravity" rule similar to the phase rule described above for two-phased systems, Palatnik extended the considerations developed for heterogeneous systems to the case of n-component, r-phased systems. For $r \leq n$, the mathematical formulation of the generalized "center-of-gravity" rule takes the form

$$m_i = M \cdot \frac{\begin{vmatrix} x_{11} \cdots x_{1,\,j-1} \, X_1 x_{1,\,j+1} \cdots x_{1r} \\ x_{21} \cdots x_{2,\,j-1} \, X_2 x_{2,\,j+1} \cdots x_{2r} \\ \cdots \cdots \cdots \cdots \cdots \cdots \\ x_{r1} \cdots x_{r,\,j-1} \, X_r x_{r,\,j+1} \cdots x_{rr} \end{vmatrix}}{\begin{vmatrix} x_{11} x_{12} \cdots x_{1r} \\ x_{21} x_{22} \cdots x_{2r} \\ x_{r1} x_{r2} \cdots x_{rr} \end{vmatrix}}$$ (69)

$$j = 1, 2, \ldots, r,$$

where M is the total mass of the entire heterogeneous system, m_j is the mass of its jth phase, and X_i and x_{ij} are the respective concentrations of the ith component in the entire heterogeneous system and in its jth phase.

Formula (69) enables us to give the quantitative characterization of multicomponent heterogeneous systems that is of importance in solution of many problems. For the case of monovariant, n-component, r-phased systems with $r = n + 1$, the relationships of the generalized "center-of-gravity" rule assume the following form [189, 190]:

$$\delta m_1 : \delta m_2 : \ldots : \delta m_n : \delta m_L = \Delta_1 : \Delta_2 : \ldots : \Delta_n : \Delta_L,$$ (70)

where

$$\Delta_L = \begin{vmatrix} x_{11} x_{12} \cdots x_{1n} \\ x_{21} x_{22} \cdots x_{2n} \\ \cdots \cdots \cdots \\ x_{n1} x_{n2} \cdots x_{nn} \end{vmatrix}$$ (71)

$$\Delta_j = \begin{vmatrix} x_{11} \cdots x_{1,\,j-1} \, x_{1L} x_{1,\,j+1} \cdots x_{1n} \\ x_{21} \cdots x_{2,\,j-1} \, x_{2L} x_{2,\,j+1} \cdots x_{2n} \\ \cdots \cdots \cdots \cdots \cdots \cdots \\ x_{n1} \cdots x_{n,\,j-1} \, x_{nL} x_{n,\,j+1} \cdots x_{nn} \end{vmatrix}$$ (72)

δm_j is a finite increment in the mass of the jth phase participating in the monovariant process and δm_L is the finite increment in the mass

of the $(n + 1)^{th}$ phase (liquid phase) with respect to which we are determining the congruence or incongruence of the transformations taking place in the system in question.

The relationships (70) of the generalized "center-of-gravity" rule enable us to determine the congruence or incongruence of the process taking place in the corresponding monovariant, n-component, r-phased system and to predict a possible outcome for it [190].

The use of a topoanalytical method based on the generalized "center-of-gravity" rule opens possibilities for further investigation of multicomponent heterogeneous systems and study and construction of their diagrams [191-193].

On the basis of this rule, Palatnik and Landau proposed, among other things, a method for determining the phase composition of n-component, r-phased systems with $r = n$, $n + 1$, $n + 2$ without isolation and chemical analysis of these phases [191]. Use of the method presupposes only knowledge of the masses m_1, m_2, ... m_r of the phases in question as obtained by $\underline{r}$ independent experiments with fixed pressure P and temperature T and various over-all component compositions over the entire corresponding heterogeneous system. As a result, the unknown concentrations X_{ij} of the phases in the system in question are determined by the following formula:

$$x_{ij} = M. \frac{\begin{vmatrix} m_1^{(1)} \dots m_{j-1}^{(1)} X_i^{(1)} m_{j+1}^{(1)} \dots m_r^{(1)} \\ m_1^{(2)} \dots m_{j-1}^{(2)} X_i^{(2)} m_{j+1}^{(2)} \dots m_r^{(2)} \\ \dots \dots \dots \dots \dots \dots \\ m_1^{(r)} \dots m_{j-1}^{(r)} X_i^{(r)} m_{j+1}^{(r)} \dots m_r^{(r)} \end{vmatrix}}{\begin{vmatrix} m_1^{(1)} m_2^{(1)} \dots m_r^{(1)} \\ m_1^{(2)} m_2^{(2)} \dots m_r^{(2)} \\ \dots \dots \dots \\ m_1^{(r)} m_2^{(r)} \dots m_r^{(r)} \end{vmatrix}} \,. \tag{73}$$

where $X_i^{(k)}$ is the concentration of the ith component throughout the system under consideration in the kth experiment and $m_j^{(k)}$ is the mass of the jth phase as determined in the kth experiment.

Combining the geometrical and analytical methods of investigating multicomponent systems in their work, and developing a generalized "center-of-gravity" rule, the above investigators went further and derived a rule of bordering regions of state (of the boundaries between regions of coexisting phases); this was formulated in the following form [192]:

$$R_1 = R - D^- - D^+ > 0. \tag{74}$$

Here, R is the dimension of the equilibrium diagram itself or of its regular section, R_1 is that of the boundary between two adjacent regions of state on the equilibrium diagram in question or on its regular section, and D^- and D^+ are the respective numbers of phases that vanish and reappear on transition of the system's figurative point through the boundary under consideration, from one region of state into the other. The rule of bordering regions of state is valid for all equilibrium diagrams of multicomponent systems and for their regular sections (provided that degeneration of the corresponding regions of state is eliminated). This rule may serve as a criterion for topological analysis of the equilibrium diagrams of multicomponent heterogeneous systems and for ascertaining their geometrical structure, and also to a certain extent as an auxiliary in interpreting experimentally obtained equilibrium diagrams of real multicomponent systems.

The use of this rule to solve such problems as those of ascertaining qualitative relationships governing the geometrical structure of the equilibrium diagrams of multicomponent heterogeneous systems and their regular and nonregular sections, determining the rules for placement of the phases in the regions of state on these diagrams, etc., is highly effective, as will be seen from the reports of Palatnik and Landau [191, 193].

The results described in the work of Palatnik and Landau, as well as the generalized formulations of the Gibbs phase rule and inequality $(r \leq n + 2)$ that they proposed and the generalized conception of nonvariant and monovariant states of thermodynamic systems that they introduced [193] are all of great theoretical interest; they also considerably facilitate experimental investigation of multicomponent hetergeneous systems, which is necessary for understanding of many complex processes that compose or accompany reactions in mixtures of crystalline solids.

§4. SUBLIMATION

Sublimation or evaporation of a crystal represents the total dismemberment of its lattice into its component elements as a result of the energy of thermal agitation. As we know, atomic and metallic crystals usually form monatomic vapor, ionic crystals produce molecules of the ionic type in the vapor, and molecular lattices evaporate in the form of molecules.

The mechanism of the evaporation process of a crystalline solid reduces to certain atoms of the superficial layer being torn away from their neighbors and carried away into the surrounding space. The possibility and even the inevitability of such dislodgement proceeds from the general principles of statistical mechanics, and in particular from the Maxwellian velocity-distribution law, which is valid for solids at high temperatures [194]. If the velocity component of some surface atom in the direction perpendicular to the surface of the crystalline solid is directed outward and is sufficiently large, then the forces attracting this atom to other atoms of the substance are unable to hold it to the surface and it flies off into the surrounding space.

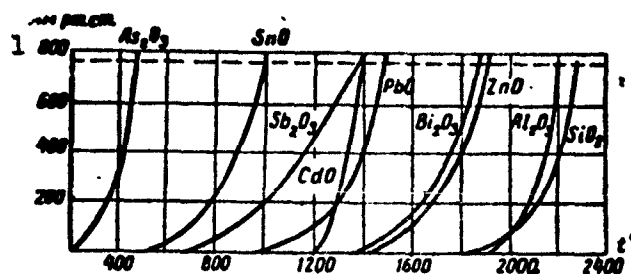The probability that an atom will be dislodged in this manner and

Fig. 34. Vapor pressures of certain
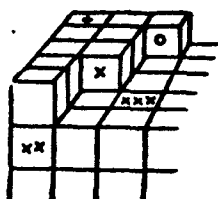oxides as as functions of temperature.
1) mm Hg.

Fig. 35. Positions of various atoms in crystal with cubic lattice.

removed into the gaseous phase is a function of the frequency and amplitude of its vibrations and, as a result, naturally depends on the temperature of the body. The vapor pressure of the body increases sharply as its temperature rises (Fig. 34). To one degree or another, however, vaporization (sublimation) of crystals takes place under any temperature conditions.

At any given temperature, different atoms on the surface of a crystal are dislodged from it at different times.* The reason for this becomes obvious when we consider the process by which an ideal crystal evaporates, using an elementary model of this crystal. The model that we shall use for this purpose (Fig. 35) has a simple cubic lattice (the atoms are represented in the form of cubes in the figure).

The energy (strength) of the bonds between various atoms of the crystal depends, as we know, on their positions. If we consider only the interaction of each atom with its nearest neighbors and denote by U the energy of interaction with each of them, then with a coordination number of 6 the bonding energy of an atom in the interior of the crystal will obviously be 6U. The energy of atom xxx (Fig. 35),

which is at the base, is 5U, while that of xx on the edge is 4U, that of atom x on an edge that has lost some of its atoms is the same as that of atom +, which is situated at a corner of the cube (3U), that of the last atom o left after evaporation of a row is 2U and, finally, that of a single atom situated at the face (not shown on Fig. 35), is U. In the evaporation (sublimation) process of a cubic crystal, the + atoms, which are more weakly bound to the crystal than the others, will be dislodged first from their positions at the corners of cubes. Then the x atoms in the row that has been affected by evaporation, which possess the same bonding energy 3U, will go into the gaseous phase. When all atoms of the row have evaporated, a "pause" intervenes and continues until the end atom in the next row is torn from the crystal, and so forth.

The vaporization process of a real crystal will obviously differ from the process described above due to the distortions of its structure.

Proceeding from the fact that the sublimation products are the same particles (e.g., atoms) that make up the initial crystalline solid, it may be assumed that the heat of sublimation expresses the difference — averaged over the entire volume of the solids — between the energy of the crystal and the energy of isolated structural elements, e.g., the atoms of its lattice, or, in other words, the averaged bonding energy of the solid's structural elements.

However, the concepts of averaged bonding energy as expressed by the heat of sublimation, and the actual bond strength (that of the interatomic bonds in particular) are not identical. A solid's heat of sublimation may not correspond to the true strength of its interatomic bonds, which is anisotropic in nature and different at various points in the solid.

Like the heat of evaporation of liquids, the heat of sublimation of crystals diminishes with increasing temperature. At the melting point, the heat of sublimation of crystals is naturally larger than the heat of evaporation of liquids by an amount equal to the heat of fusion.

Let us devote brief consideration to the kinetics of the sublimation process.*

The rate of evaporation or sublimation of a spherical particle without restriction as regards influx of heat may be (see [196, 197]) expressed by the equation

$$U = 4\pi r D \ln \frac{P - P_0}{P - P_n}. \tag{75}$$

where r is the particle radius, D is the coefficient of diffusion, P is the total gas pressure above the particle, P_0 is the partial vapor pressure of the particle substance at a certain distance from its surface, and P_n is the saturation vapor pressure of this substance at the vaporization temperature (pressure at surface of evaporation).

If the process takes place at constant temperature and pressure, all terms of Eq. (75) except the radius r and the pressure P_n will be constant. Expressing the quantity of evaporated material G in fractions of unity, we may write that

$$r = R(1 - G)^{\frac{1}{3}}, \tag{76}$$

where R is the initial radius of the particle.

The saturation vapor pressure P_n of a spherical particle is, as we know, a function of its radius. From the standpoint of the molecular-kinetic theory, this is accounted for by the increase in the work of moving a molecule from the condensed phase into the gaseous phase as the radius of curvature of a convex interface increases.

- 142 -

This relationship proceeds [5] from the equation

$$P_\bullet = P_{n_0}\left(1 + \frac{2M\sigma}{rR_g Td}\right),\qquad\qquad(77)$$

where P_{n_0} is the equilibrium vapor pressure at a temperature T above a flat surface of a substance of molecular weight M and density $\underline{d}$, P_n is the same pressure above a particle of this substance having a radius $\underline{r}$, R_g is the gas constant and σ is the surface tension.

This equation is equally valid for vaporization from the surface of a liquid droplet [198] and for sublimation from the surface of a spherical solid particle [199-201].

In theory, therefore, as the radius $\underline{r}$ of the particle decreases, the pressure P_n of the vapor above its surface must increase. The practical significance of this increase in P_n with diminishing $\underline{r}$ may be inferred from the following data.

The dependence of P_n on $\underline{r}$ is perceptible at very small values of $\underline{r}$ (of the order of 10^{-6} cm), while in real powder mixtures we deal with radii of the order of 10^{-2} to 10^{-3} cm.

For water at room temperature and with a drop radius $r = 0.1$ mm,

$$P_\bullet = P_{n_0}\left(1 + \frac{2 \cdot 18 \cdot 73}{0,01 \cdot 8,31 \cdot 10^7 \cdot 290}\right) \approx P_{n_0}(1 + 10^{-5})$$

(here $\sigma = 73$ dynes/cm at $18°$ and $R_g = 8.31 \cdot 10^7$ ergs).

In exactly the same way, we find that with $\underline{r}$ equal to 0.001 and 0.0001 mm, the respective ratios $P_n : P_{n_0}$ are 1.001 and 1.01. In other words, as the radius of the water droplets changes from 10^{-4} to 10^{-5} cm, i.e., by a factor of 10, the pressure P_n changes by approximately 1% (see also [60]). Thus, the change in P_n is extremely small even for a large change in $\underline{r}$.

Since the ratio $r:R$ is equal or proportional to the cube root of the relative amount of residual (unevaporated) material, we find, for example, for 98% sublimation of the spherical grain, $r = 0.272R$, i.e.,

the radius changes by a factor of less than four as compared with the original value.

To supplement the above, it should be noted that in Eq. (75), the pressure P_n appears in a fraction after the natural logarithm symbol.

It follows from the above that for ordinary powder mixtures, the dependence of P_n on the grain radius is negligibly small in the overwhelming majority of cases. On this basis, Eq. (75) may be rewritten is follows for constant temperature and total pressure:

$$U = \frac{dG}{dt} = f(r) = K'r. \qquad (78)$$

where G is the quantity of evaporated material, or, in other words, applying Eq. (76), in the form

$$\frac{dG}{dt} = K'R(1 - G) . \qquad (79)$$

The rate of evaporation or sublimation of matter from a mass of grains of initial radius R is proportional to their number N per unit weight of this mass:

$$\frac{dG_1}{dt} \sim R(1-G)^{\frac{1}{3}} N. \qquad (80)$$

where G_1 and G are the absolute (for example, in grams) and relative (in fractions of unity) quantities of the evaporated material, respectively, $\sim$ is the proportionality sign and

$$N = \frac{1}{\frac{4}{3} \pi R^3 \gamma} = K''R^{-3}.$$

if γ is the apparent specific gravity of the grain (material).

Finally, the rate of evaporation or sublimation of a mass of spherical particles is

$$\frac{dG}{dt} = K'''R^{-2}(1-G)^{\frac{1}{3}}. \qquad (81)$$

- 144 -

or, after substituting $K'^"R^{-2} = K$,

$$\frac{dG}{d\tau} = K(1-G)^{\frac{2}{3}}. \tag{81a}$$

Obviously, as $G \to 0$, the rate of sublimation $dG/d\tau \to K$, i.e., with small relative quantities of evaporated (sublimated) matter, the time variation of the evaporation (sublimation) rate may be practicall₃ unnoticeable.

Integration of Eqs. (81) and (81a) with the initial conditions $G = 0$ and $\tau = 0$ results in the respective equations

$$F(G) = 1 - (1-G)^{\frac{2}{3}} = K^"R^{-2}\tau, \tag{82}$$

$$F(G) = 1 - (1-G)^{\frac{2}{3}} = K\tau. \tag{83}$$

Equation (82) characterizes the relative quantity of evaporated matter as a function of the initial particle radius for varying process times. In the case of evaporation from a flat surface (e.g., from the surface of a tablet), the values of all terms in Expression (75) for the rate of the process undergo no change under isothermal conditions, and accordingly the rate of the process remains virtually constant over a long span of time:

$$\frac{dG}{d\tau} \approx K.$$

Strictly speaking, a gradual change in the rate of the process may take place in the case of tablet evaporation as a result of the gradual decrease in the evaporation surface.

§5. BASIC TYPES OF TRANSFORMATIONS IN SOLID SUBSTANCES. POLYMORPHISM

The chemical composition of the phases that arise in the process in which crystalline substances are transformed may differ from the composition of the initial phases or be identical with it. Since this likeness or unlikeness has a considerable effect on the qualitative laws governing the corresponding processes, we distinguish between

- 145 -

two types of transformations in solids:

1) those that take place without changes in the chemical composition of the phases;

2) those accompanied by the appearance of phases with modified chemical composition.

Processes of the former type amount to changes in the crystal structure of the material only, so that the appearance and growth of seeds of a new phase are considerably easier in them. An important stage in processes of the second type is diffusion of at least one of the system's components in a layer of the initial phases or new formations. This is the chief factor behind the differences in the qualitative laws governing the two types of processes.

Nevertheless, literature characterizations of processes of the first type as nondiffusive to distinguish them from the "diffusive" processes of the second type are not sufficiently rigorous, since diffusion of crystal-lattice elements may, as we know, take place and even become a major factor, even in those cases where the chemical composition of the material does not change in the process of its transformation.

Processes of the first type include polymorphic transformations and the phenomena of ordering and disordering of solid solutions. Some of these processes take place at such high rates — which are occasionally difficult to measure — that they were at one time incorrectly regarded as "seedless."

All other transformations of crystalline substances, including, of course, chemical reactions in mixtures of them, are processes of the second type.

Among the processes that take place without changes in the chemical composition of the original phases, two types of phase transitions

should, according to Erenfest,* be distinguished.

In transitions of the first kind, a change in the solid's crystalline structure and in the first derivatives of its thermodynamic potential with respect to temperature and pressure, i.e., the entropy $S = -\partial Z/\partial T$ and volume $V = \partial Z/\partial p$ and, consequently, the energy E, takes place abruptly at a certain temperature and is accompanied by a marked heat effect. Here, the change in the thermodynamic potential $Z = E - TS + pV$ obviously remains continuous.

A certain temperature curve of thermodynamic potential is peculiar to each modification of the substance. At a certain temperature, the thermodynamic-potential curves of the initial and new phases intersect, just as do the curves of their vapor pressures (Fig. 36): the thermodynamic potentials of the two phases are the same and the phases are at equilibrium. Above a certain temperature, one modification is stable, and below it the other modification is stable.**

At a given pressure, therefore, each modification of the material is stable in a certain temperature range. Transition of the substance into another modification takes place at the boundary of this temperature range of stable existence for each of the various modifications (normally known as the transformation point).***

In phase transformations of the second kind, the object of basic researches by Landau and Livshits [5, 202, 203], the thermodynamic potential Z and its first derivatives (entropy and volume) change continuously, while the second derivatives of Z with respect to temperature and pressure change discontinuously.

Due to the continuity of the entropy variation in the transition process, no liberation of or absorption of heat takes place. Due to the stepwise change in the second derivatives of Z with respect to p and T, however, the quantities expressed by these derivatives, such
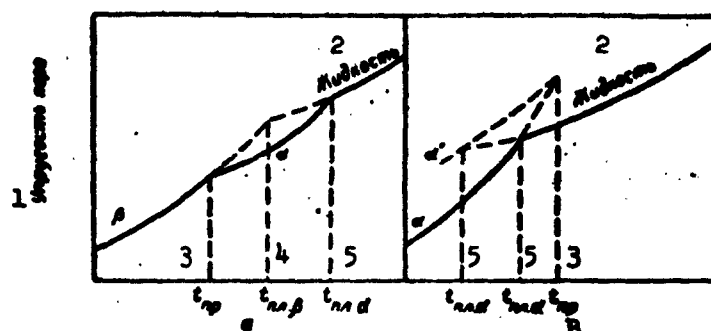
Fig. 36. Vapor pressure as a function
of temperature in cases of enantiotropic
transformation (a) and monotropic trans-
formation (b). t_{pr})temperature of the
transformation into the other modifica-
tion; t_{pl}) melting point; the broken lines
indicate unstable states. 1) Vapor pres-
sure; 2) liquid; 3) t_{pr}; 4) $t_{pl.\beta}$; 5) $t_{pl.\alpha}$.

as heat capacity, coefficient of thermal expansion and compressibility
coefficient also change stepwise (naturally, they can also change
stepwise in transitions of the first kind).

In transformations of the second kind, the solid (lattice)
moves from one modification to another during heating by a series of
small stepwise changes that take place over a certain interval of
temperatures. Thus, although discontinuity of the process is in princi-
ple retained in this case, the solid moves progressively into its
new state, so that at temperatures near the transition point the
new modification differs negligibly from the old modification. At the
transition point, the compositions of the two phases coincide or, in
other words, all of the material is in the same state. In this respect,
phase transitions of the second kind are, for all practical purposes,
continuous.

The transformation of barium titanate may serve as an example of
this type of transition. At high temperatures, $BaTiO_3$ has a cubic

- 148 -
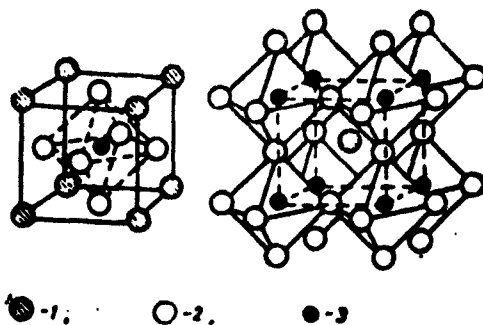
Fig. 37. Crystal lattice of barium titanate.
1) Ba^{2+}; 2) C'; 3) Ti^{4+}.

lattice with the cell shown in Fig. 37. On cooling of such barium titanate below a certain temperature, the Ti and O atoms begin to shift with respect to the Ba atoms, moving toward one of the edges of the cube. This displacement is effected continuously, but even a small shift of this type results in a change in the symmetry of the lattice. Actually, as soon as such a shift begins, the lattice symmetry changes immediately from cubic to tetragonal. Here, there is no discontinuity in the change of the solid's state.

Since the states of the two phases at the point of such a transition are the same, the symmetry of the solid in this state contains all elements of symmetry of both phases, although one of them is always higher than the other in phase transitions of the second kind. In contrast to transitions of the first kind, we do not have to speak here of a minimum or of equality of the phase thermodynamic potentials.

A corollary of the special properties of transitions of the second kind is the impossibility of supercooling or superheating of the solid during them, as is frequently observed in processes of the first kind.

As was shown by Landau [202], a phase transition of the second kind is impossible between a liquid and a crystalline solid.

In practice, however, we frequently encounter phase transitions of both the first (see, for example, below on the polymorphic transformations of silica) and the second kind (many processes of ordering and disordering in solid solutions [203 and others]) on heating of crystalline solids.

All of these processes, and transitions of the second kind in particular, have as yet been the subject of little theoretical or experimental study.

* * *

Certain substances have the ability to crystallize in different lattices under different conditions.

This phenomenon, which is known as polymorphism, has been established for carbon, sulfur, iron, tin, zinc sulfide, aluminum oxide, silicon dioxide, titanium dioxide, calcium carbonate and many other substances.

Since the properties of a substance are determined to a considerable degree by the nature of its crystal structure, the various crystalline modifications of a substance having a given chemical composition possess different properties.

The differences in the properties of two well-known modifications of carbon (graphite and diamond) may serve as an extremely simple and clear example of this proposition. Graphite belongs to the hexagonal syngony, is opaque, black in color, and soft, and has a specific gravity of 2.22 and is an excellent conductor of electric current. Diamond belongs to the cubic syngony, is transparent, has a Mohs hardness of 10, a specific gravity of 3.51, and is a dielectric.

The crystal structures of polymorphic modifications may be distinguished from one another by their coordination numbers (e.g., the coordination numbers of β- and γ-iron are 8 and 12, respectively), by

the type of closest packing in the case of identical coordination numbers (e.g., cubic in TiO_2-anatase, hexagonal in TiO_2-rutile, and four-layered in TiO_2-brookite), by the placement of the atoms of one of the elements (columbite and mossite), by the angles formed by structural groups (the Si-O-Si angle is $180°$ in cristobalite and $160°$ in quartz) and, finally, by the angles of rotation of molecules or radicals in the lattices (paraffins).

As was noted above, atoms (molecules, ions) of a substance always tend to form a stable lattice possessing the smallest free-energy reserve.

Since this free-energy reserve depends on certain conditions, one modification may be stable under one set of conditions and another modification under another set. A change in conditions, principally in temperature or pressure, may result in a change in the crystal lattice, i.e., in a transition of the substance from one crystalline modification into another that is stable under the new conditions.

Greater practical importance is generally ascribed to those processes of transformation in crystalline solids that take place at constant (atmospheric) pressure.

The process in which one modification is transformed into another is similar in many respects to the process of transition from the solid state into the liquid state or vice versa. The difference consists in the fact that in fusion, for example, the ordered arrangement of particles in the crystal lattice is supplanted by a less ordered arrangement in the melt, while in a polymorphic transformation one rigorous ordering of the particles is replaced by another.

In this replacement of one order by another, the atoms do not change positions, but are simply shifted with respect to one another by distances not in excess of the interatomic distance. However, these

- 151 -

displacements and changes in the relative positions of the material's particles naturally involve expenditure or evolution (liberation) of a certain amount of energy.

This gives rise to the concept of the heat of a polymorphic transformation — the quantity of heat absorbed or liberated on transformation of a unit mass of substance. The value of this heat depends on the structure and cohesive forces of the particles forming the initial and final crystals, and varies over a wide range for different transformations.

To execute a transition from a state with a larger free energy to a state with a smaller free energy in a polymorphic transformation, the atoms must pass through intermediate states with elevated energies, i.e., they must overcome certain energy barriers. To do this, they must obviously possess an energy adequate to overcome such barriers. The availability of this additional energy is conditioned by the non-uniformity with which the energy of thermal agitation of the atoms is distributed. The probability of such an event is determined by the ratio of the height of the barrier to the average vibration energy.

When a solid goes from one lattice to another, some layer of atoms belongs jointly to the old and new lattices. Thus, there is an elastic relationship between them. As a result, enormous shearing stresses and the corresponding elastic deformations arise.

Under any given set of conditions, the energy of the new modification will be smaller than that of the initial modification: as was noted atove, the process goes toward a reduction of the system's free energy.

In the case of the so-called directional migration of atoms with retention of the bonds between the old and new lattices, continuous transition of the solid into the new modification may result in the

appearance of a particularly large elastic-deformation energy. The result may be either plastic deformation of the system as a result of attainment of the elastic limit or stoppage of the transformation process, since further progress in it would involve a rise in the system's free energy, make it necessary to overcome higher energy barriers, and require a larger energy of activation and a larger thermal-agitation energy.

Two forms of polymorphic transformation exist: <u>enantiotropic</u> or <u>reversible</u> processes, which go in either direction at the temperature of transition, and <u>monotropic</u> or <u>irreversible</u> transformations, which proceed only in one direction.

The former are characterized by the presence and the latter by the absence of a rigorously determined temperature for the process (transformation point). The β-quartz $\rightleftarrows$ α-quartz and α-quartz $\rightleftarrows$ α-tridymite transformations may serve as an example of the enantiotropic type, and the transition of diamond into graphite as an example of the monotropic type. At enantiotropic points, the process by which the substance is converted into another modification is, in accordance with Le Chatelier's principle, accompanied by absorption of heat if it takes place on heating (like melting) and by evolution of heat if it takes place on cooling (like crystallization from the melt).

The monotropic transformation of a low-temperature modification into a high-temperature modification may be accompanied by the evolution of heat.

To a greater or lesser degree, the crystalline modifications of a substance may be distinguished from one another on the basis of their structures and physical properties.

The varieties of silica are broken down into two categories on the basis of this criterion: first-order varieties - quartz, tridymite

and cristobalite, which differ sharply from one another, and those of the second order - the α-, β- and γ-forms of the above varieties. Within the limits of a given variety, the structural and property differences between these forms are relatively minor. Accordingly, the heat effect of second-order transformations (of one form into another within the limits of the same variety) is relatively small as compared with the corresponding figures for transformations of the first order.

As a result of changes in the properties of the substance in polymorphic transformations, these processes are reflected in the temperature curves of the substance's volume, optical constants, heat capacity and vapor pressure. Among other things, a lower vapor pressure (and a higher melting point) naturally corresponds to the modification that is more stable at the temperature in question, i.e., that which possesses the smaller free energy, in accordance with the second law of thermodynamics. Curves of this type (temperature-versus-property) are presented below in our description of single-component systems (SiO_2, Al_2O_3 and others). It is clear from what we said above that we may observe a break and even a horizontal plateau on the heating curve of a substance at its transformation point (Fig. 38).
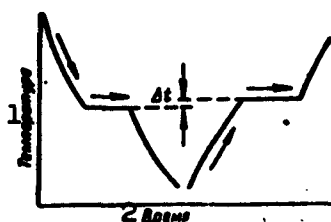
Fig. 38. Cooling and heating in enantiotropic transformations.
1) Temperature; 2) time.

The little-studied question as to the rate of polymorphic transformations is important. It is known that the energy-absorbing processes (of the first order), which involve an essential change in the crystalline structure, proceed at lower speeds than processes of the second order. Sometimes, particularly at low temperatures, the transformation rate is so low that the high-tempera-

ture modification can be greatly supercooled (in much the same way as liquids are supercooled), or the low-temperature modification may be superheated (in contrast to the virtually impossible superheating of a solid above its melting point) with respect to the transition point without the transition taking place. In these cases, both modifications may exist at the same temperature, but, like a supercooled liquid, the solid is in a thermodynamically unstable, so-called metastable state. It may arise in the same way as the intermediate stage in the process in which the substance goes from the unstable to the stable state. As we know, transformation of an unstable system into a stable system takes place progressively, by degrees (Ostwald's rule). The metastable state may be disturbed by introducing a primer into the solid; these are particles of the modification that is stable at the temperature in question. Apparently, other substances can also perform the function of such a primer. It is known that a small crystal of a substance that is isomorphic with the substance in supersaturated solution may seed crystallization of this dissolved material. It may be assumed in analogy with this that in cases of polymorphic transformation, a substance that is isomorphic to the stable modification may excite (or accelerate) the transition of the unstable modification into the stable modification. However, such excitation or acceleration of the process with the aid of primer is observed in far from all cases (see pages 187, 188).

Addition of insignificant quantities of certain substances to a substance that is undergoing a polymorphic transformation delays this process. These process-delaying materials thus act as stabilizers for the initial modifications.

Investigation of the kinetics of polymorphic transformation processes must obviously be based on analysis of their essential physical

nature. Like any other process in which a crystalline phase appears, each such process consists of two phenomena: seeding of crystallization centers and the growth of crystals of the new phase. The transformation rate here is a function of these two factors, which vary differently in accordance with the temperature, duration and other conditions of the process. From an energy standpoint, growth of the crystal should proceed more easily than seeding, which requires the work of interface formation. The activation energy of seeding is usually somewhat higher than the activation energy of growth.

The number of grains of the new phase will naturally be proportional to the rate at which they are seeded; their size will depend on the growth rate. In this connection, it is essential to note two circumstances:

1) the higher the degree of superheating or supercooling, the smaller will be the critical seed size and the larger the number of seeds;

2) at sufficiently high temperatures (at any given temperature), the growth rate will be higher than that of seeding.

Obviously, polymorphic transformation processes are of great industrial significance in connection with the stepwise change that occurs in the properties of substances on such transformations and the large and often repeated changes in temperature of many (e.g., refractory) materials in their practical applications.

Manuscript Page No.	[Footnotes]
70	*E_1 and E_2 are usually expressed in cal/mole.
75	*To avoid the need to deal with very small numbers the values of D are often expressed in cm^2/day.

84   *The concentration dependence of the diffusion coefficient is "thrown out" only in the case of self-diffusion.

94   * Much is as yet unclear concerning the role taken by surface diffusion in the sintering process. Indications of a considerable importance for it can be found in the literature. However, analysis of voluminous experimental data indicates that surface diffusion is really subordinate in importance: it may make itself felt to a certain degree in the sintering process only in its early stages and at very small a [83, 125].

102   *See, for example, the paper by F. Sauerwald, Aktuelle Probleme Phys. [Pressing Problems of Physics] (Pub. E. Thilo), Berlin, 1953; F. Wolf and H. Ritzmann, Chemie-Ing. Technik [Chemical Engr.-Technician], No. 8, 516 (1958) and the references cited in this paper.

106   *Concerning sintering in the presence of a liquid phase, see Kingery, W.D., Ceramic Fabrication Processes, New York, 1958, page 131.

117   *The Frenkel' theory [44, 45] explains why a solid does not melt in some appreciable temperature range.

128   *Assuming for simplicity that mixture formation and phase transformations are not accompanied by a change in volume, we may use the free energy in first approximation instead of the thermodynamic potential.

140   *Stranskiy [195] made a detailed study of this problem.

142   *This problem was considered in 1952-1954 by one of the present authors in References [231, 398 and others]. The recently published report of N.A. Fuks entitled Ispareniye i rost kapel' v gazoobraznoy srede [Evaporation and growth of drops in a gaseous medium] (Acad. Sci. USSR Press, 1958), which casts light on the results of the most important research into both of these processes, is of great interest to study of this problem.

147   *P. Erenfest, Proc. kon. Akad. [Proc. Roy. Acad.], Amsterdam, 36, 153 (1933).

147   **Strictly speaking, all this is correct when the diffusion processes are "blocked," i.e., do not occur, and only rebuilding of the lattice without changes in the concentration of the solid solution can proceed.

147   ***The conditions and laws of several such transitions are considered in §1 of Chapter 9.

[List of Transliterated Symbols]

72   в = v = vakansiya = vacancy
72   y = u = uzel = lattice point

99	к = k = kapillyarnyy = capillary
110	рекр = rekr = rekristallizatsiya = recrystallization
110	пл = pl = plavleniye = melting
123	т = t = tverdiy = solid
123	ж = zh = zhidkiy = liquid
130	э = e = evtektika = eutectic
142	н = n = nasyshchenyy = saturated
143	г = g = gazovyy = gas
148	пр = pr = prevrashcheniye = transformation

Chapter 3

MECHANISM OF REACTIONS IN MIXTURES OF SOLIDS

§1. GENERAL PREMISES. "ELEMENTARY" PROCESSES

As we know, a chemical reaction in a mixture of crystalline reagents has a number of important special properties: it takes place at the interface between coexisting phases, i.e., it is heterogeneous in nature; like any topochemical reaction, it depends on the spatial positions of the masses of the reacting components and results in the appearance of phases of a new (modified) chemical composition, i.e., is, in the final analysis, a transformation of the second type (page 146); it consists of a series of elementary processes, which may also include transformations of the first type.

To ascertain the nature and sequence of these processes, Huetting [204, 205] once undertook a circumstantial investigation of reactions in mixtures of powdered oxides of various metals as the temperature was progressively raised. He observed a change in the composition and properties of the mixtures on x-ray diffraction patterns, on the basis of dye and water-vapor sorption, the catalytic action of the mixture on certain reactions, its magnetic susceptibility and fluorescence, and with the aid of certain other methods. Particularly detailed study was devoted to the reaction of zinc oxide with ferric oxide.

On the basis of his investigation, Huetting concluded that the process in which the reagents react in the above mixture and in many other crystalline mixtures may be broken down into six periods:

a) coating;

- 157 -

b) activation as a result of "quasi-molecule" formation and formation of superficial molecular films;

c) deactivation of the molecular surface films;

d) activation as a result of internal (bulk) diffusion;

e) formation of a crystalline reaction product and

f) correction of defects in the crystal lattice of the compound that has been formed.

The coating period is characterized by contact between the surfaces of the materials; this is accomplished as soon as they are mixed and becomes more extensive on heating. The dye-adsorption capacity (curve 1, Fig. 39) diminishes during this stage, as it does in the subsequent course of the process. By using a dye that adsorbs selectively, we may establish that one of the reacting components "coats" the other. The substance having the lower melting temperature is usually the "coating" component.
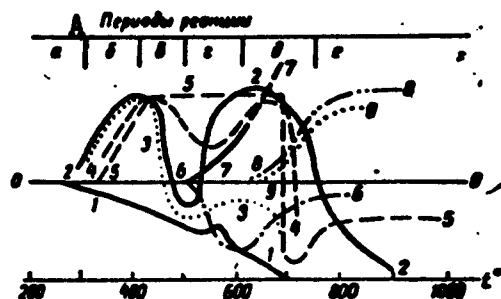
Fig. 39. Change in properties of ZnO + Fe_2O_3 mixture in process of heating. 1) Absorption of dye; 2) catalytic effect on reaction $2CO + O_2 = 2CO_2$; 3) rate of water-vapor sorption; 4) catalytic effect on reaction $2N_2O = 2N_2 + O_2$; 5) color (on Ostwald scale); 6) density; 7) magnetic susceptibility; 8) intensity of $ZnFe_2O_4$ lines on x-ray diffraction patterns; 9) fluorescence. A) Periods of reaction.

Period of activation as a result of "quasi-molecule" formation and formation of superficial molecular films. In the case of a mixture of zinc oxide with ferric oxide, this period ($300°-400°$) is characterized by an increase in the catalytic action of the mixture (curve 2) on the reaction $2CO + O_2 = 2CO_2$ (at a temperature of $250°$), the rate of water-vapor sorption (curve 3) and the catalytic effect on the reaction $2N_2O = 2N_2 + O_2$ at a temperature of $510°$ (curve 4),

- 158 -

and by a change in color on the Ostwald scale (curve 5).

Period of deactivation of superficial molecular films. For a mixture of zinc oxide with ferric oxide, this period occurs at 400-500°. It is accompanied by an increase in the bonding strength in the superficial film with the result that the activity of the reacting mixture diminishes. In certain mixtures, e.g., magnesium oxide and ferric oxide, this period is not observed.

Period of activation as a result of internal (bulk) diffusion. (or onset of general transposition). Here, the particles of one component may begin to change places within their own lattice and diffuse into the crystal lattice of the other component. For the mixture of zinc oxide and ferric oxide, this period intervenes at a temperature of 500-620° and is characterized by an increase in the catalytic effect, first on the oxidation reaction of carbon dioxide, and then on the decomposition of nitrous oxide. Here, the density (curve 6, Fig. 39) begins to diminish while the magnetic susceptibility (curve 7) increases. However, no distinct lines of the new compound are as yet discernible on the powder-diffraction pattern.

The period of formation of the crystalline reaction product occurs in cases where, as a result of continued diffusion, the concentration of the solid solution (more precisely, the disordered mixed phase) of one component in the other attains such a magnitude that it becomes possible to isolate crystals of a new compound. For the mixture under consideration, thes period intervenes at a temperature between 620° and 750°. Thereupon the catalytic effect of the reaction mixture increases. The first lines of the reaction (zinc ferrite) make their appearance on the powder diagram; their intensity (curve 8, Fig. 39) increases steadily in exactly the same fashion as the difference between the fluorescence intensities (curve 9) of the pure zinc oxide

and the reaction mixture (given identical thermal processing).

Period of correction of structural defects in crystal lattice of newly formed compound. At first, the crystals of the new compound still possess structural defects, but these disappear for the most part as the temperature is raised further and the x-ray diffraction patterns of this compound become normal. A further increase in temperature results in collective recrystallization of the compound that has formed. Heating to very high temperatures does not exclude the possibility of decomposition of the newly formed compound (this phenomenon occurs, for example, when tricalcium silicate is heated to temperatures above 1900°). In view of the considerable difficulty encountered in experiments at very high temperatures, the general qualitative laws governing such processes have not yet been adequately studied.

It has been established by numerous investigations carried out since the work of Huetting described above that the process of physicochemical transformation in a solid mixture, which takes place not only under the conditions of gradual heating, but also at constant relatively high temperature, is usually rather complex. It may incorporate the following basic "elementary" processes or stages:

1) the appearance of defects and "softening" of the crystal lattices;

2) reconstruction of the lattices as a result of polymorphic transformation;

3) formation and decay of solid solutions;

4) diffusion (external, internal, superficial);

5) sintering, "relaxation," recrystallization;

6) fusion, solution of system components in melt;

7) crystallization from the liquid phase;

8) sublimation;

- 160 -

9) dissociation;

10) the chemical reaction proper.

Some of these "elementary" processes* are inevitably interrelated (e.g., 5, 7 and 8 with 4) while others (e.g., 3 and 4) may, in general, be encountered "in pure form", i.e., independently; some "elementary" processes (such as 4, 10) are necessary stages of any reaction in a solid mixture, while others (e.g., 2, 3, and 8) may also accompany it as parallel processes or not occur at all in the course of the reaction.

It is clear, however, that to understand the essential nature of the reactions taking place on heating of mixtures of crystalline re-agents and the qualitative laws governing them it will be necessary to study the mechanism and laws of all the "elementary" processes listed above and their interrelationships under practical conditions.

It is therefore essential to note that, as was indicated above (Chap. 2), each such process is in itself a combination of a number of simpler phenomena and that certain "elementary" processes, such as, for example, 2, 3, 4, 5 and 7, are complex and have been the subject of far from adequate study. However, as a result of the labors of Fol'me Kurnakov, Tammann, Frenkel', Bochvar, Danilov and other investigators, the most important qualitative laws governing them have now been es-tablished (to a certain extent in approximate form), so that there is a possibility of more or less purposive control of the these processes and the reactions that they compose in crystalline mixtures, and of studying the mechanism of such reactions successfully.

One of the basic problems encountered in this suudy is that of ascertaining the physical state of the initial reagents, impurities, intermediate compounds, and final products in the reaction process. In the literature, the reactions of which we are speaking here are most frequently referred to as solid-phase reactions. In the strict sense

of the word, "solid-phase" implies a reaction accomplished due to direct interaction between the grains of crystalline reagents (i.e., one that takes place in the solid phases) without any participation of liquid or gaseous phases.

In actuality, many processes in which crystalline mixtures are transformed under conditions that are of technical interest take place with the participation of gases and liquids. When crystalline mixtures are heated, processes of this type may also accompany the strictly solid-phase reactions, unfolding simultaneously with them or before or after them. Here, the detection of small quantities of liquid and gaseous phases and determining their role in the reactions under consideration is sometimes a matter of considerable difficulty. As a result, the question as to the role of liquid and gaseous phases in the mechanism of certain reactions has not yet been definitely ascertained.

In general, a reaction between two crystalline substances may take place both by direct interaction between them in the absence of liquid and gaseous phases and with participation of these phases. Here, it is also possible for substances in one or two, or, finally, three physical states to participate in the process simultaneously. If under certain definite conditions the reaction may take place either with or without participation of liquid or gaseous phases, it will proceed preferentially along the second path in the overwhelming majority of cases.

It can obviously be stated that a process is taking place with the participation of substances present in only one physical state if it has been proven that substances present in other physical states are not factors in this process. As a consequence, proof of the possibility or even of the distinct importance of, for example, direct in-

teraction between the solid substances in a given process (to which many investigations were at one time devoted) is not sufficient to negate the essential importance of other phases in this process.

To understand the true mechanism of the reactions under consideration, we should proceed from the basic possibility of participation in them of substances present in the solid, liquid and gaseous phases in evaluating their importance in these reactions on the basis of detailed analysis. In such analysis, the basic physicochemical properties of the reactions under consideration, as noted above, and the special features of the physical situation in which they unfold in various specific cases must be taken into account.

In view of the heterogeneous nature of these reactions, the most important quantity determining, among other quantities, their rate and, accordingly, the yield of product, is the area of the reaction surface between the reagents.

In this connection, we note that the area of direct contact between the grains of a loose-poured powder is reckoned in millionths and even ten-millionths of their total surface (page 51). Irrespective of this, it is possible in the majority of cases for the grain surfaces of each of the reagents to be fully exposed and accessible to attack by the other reagent or reagents only at the very beginning of the process (at $\tau = 0$). As the process advances, the grains of one (most frequently) of the reagents are covered by a more or less dense layer of reaction product, the thickness of which increases continuously in the course of the reaction.

We may distinguish two groups of processes related to the formation of this layer.

The first of these includes processes in which the reaction product has a volume smaller than that of the reacted reagent, on the

grains of which the layer in question grows. In this case, the layer of product is porous and loose and does not offer any particular resistance to penetration of the second reagent into the reaction zone.

The second group includes processes in which the volume of the product that forms is larger than the volume of the reacted "coated" reagent so that the layer of product is dense and free of microscopic pores, and the subsequent course of the process involves diffusion of one reagent to the other through this layer.

Obviously, the rate of processes of the second group is limited to a considerably greater degree by the resistance of the product layer and should be considerably lower than that in processes of the first group, although this rate naturally diminishes with time in all cases.

The essential difference between these two groups of processes that we are considering was noted as early as 1923 [206].

The nature of the layer's resistance is readily estimated mathematically in first approximation.

Thus, if G_r and G_p are, respectively, the weights of the reagent and that of the product obtained from it (in accordance with the equation of the reaction), and γ_r and γ_t are the specific gravities of the reagent and the product, then given a reagent volume G_r/γ_r, the volume of the product will be G_p/γ_p.

Obviously, if $G_p/\gamma_p > G_r/\gamma_r$, the layer is dense, while it is porous if $G_p/\gamma_p < G_r/\gamma_r$. Deviations from this rule are sometimes observed in practice. A theoretical explanation for these deviations has been given by Frank and van der Merve [207], according to whose reasoning the newly formed layer has the lattice parameters of the initial substance only when the difference between their molar volumes is < 15%. If this difference exceeds 15%, the newly formed product may peel

- 164 -

from the surface of the initial solid, and this will naturally result in porosity.

Inferences as to the nature of the layer directly from the relationships between the densities of the product and the initial material, which are frequently encountered in the literature, are less rigorous and well-based, although in individual cases, e.g., in evaluating the properties of oxide films on certain metals [89, 208], such inferences result in correct conclusions.

§2. TAMMANN-KHEDVAL THEORY. KURNAKOV THEORY

Systematic study of the mechanism of reactions in mixtures of solids was begun approximately thirty years ago by the work of Khedval [209, 210], Tammann [211-213] and their colleagues. Recording the heating curves of the initial mixtures and the final products (Fig. 40), Khedval and Kheyberger [209] observed the so-called exchange reactions of acid radicals, which take place between crystalline metal oxides and salts of oxygen-containing acids in accordance with the reaction

$$MeO \quad Me'RO_n \rightarrow Me'RO_n + Me'O.$$
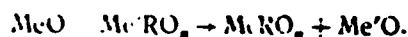
Using the same method, Tammann et al. [211, 212] investigated numerous reactions of acidic oxides with basic oxides, reactions of metals with sulfates, nitrates, sulfides and metals, and those of salts with metals.

On the basis of their investigations, Tammann [211] and Khedval [214] formulated a series of fundamental conclusions concerning the mechanism and specific qualitative laws of reactions in crystalline mixtures.

These conclusions can summed up as follows:

1. Reactions that arise in mixtures of crystalline solids, such as salts of oxygen-containing acids, and oxides, basic and acidic ox-

ides, metals and oxides, sulfides and metals, sulfides and oxides, and so forth, take place on heating by direct interaction between the grains of these solids. Any essential participation of liquid and gaseous substances in these reactions is excluded.

Reactions between solids take place with evolution of heat. In other words, only exothermic reactions are possible between solids.

Attainment of equilibrium in systems that do not contain solid solutions is practically impossible. In the absence of solid solutions, the equilibrium state can intervene as such reactions unfold only at certain values of the process temperature and provided that the heat of reaction is very small, while the sum of the heat capacities of the initial substances and the reaction products must differ considerably (the probability of which is very low).

The temperature at which the reaction begins corresponds to the temperature at which the crystal lattice elements of the reagents exchange places at a high rate and to their sintering temperature (is identical to this temperature). The temperature at which a reaction begins between an oxide and a salt ("acid-radical exchange reaction") then is determined by the mobility of the oxide's crystal-lattice elements.

In the case of polymorphic transformation of the mixture components at a relatively low tmmperature (a temperature lower than that of the reaction in the absence of such a transformation), chemical reaction begins and progresses rapidly at the point of this polymorphic transformation.

When crystalline solids are heated, liquid may appear as a result of melting and gas chiefly as a result of sublimation and dissociation of the solids. These phenomena are not essential factors in strictly solid-phase reactions, which are accomplished by direct interaction
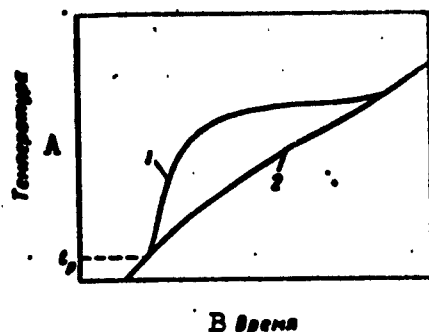
- 166 -

Fig. 40. Heating and cool-
ing curves in an exothermic
reaction in solid mixture.
1) Heating of initial mix-
ture; 2) cooling of reac-
tion product. t_r is the
reaction temperature.
A) Temperature; B) time.

between the crystalline solids.

3. According to Tammann and Khed-
val, the following may serve as proofs
of the decisive role taken by direct
reaction between the solid phases in
the mechanism of chemical transforma-
tion of solid mixtures:

1) the occurrence of a reaction
between the dry reagents;

2) the occurrence of the reaction
at temperatures lower than the melting
points of the initial reagents and
those of the eutectics possible for the system;

3) the impossibility of spontaneous heating (and the resulting
fusion) of the reagents by the heat of reaction before the reaction
begins;

4) the occurrence of the reaction at temperatures at which the
formation of gas by decomposition or sublimation of any reagent is
virtually unnoticeable or takes place at a negligible rate;

5) the practical constancy of the reaction temperature of a given
oxide with different salts, and salts of oxygen-containing acids in
particular;

6) the absence of a link between the temperature of "considerable
rate" of the dissociation of a given salt and the "noticeable rate"
temperature of its reaction with an oxide;

7) the insignificance and, in many cases, absence of influence
exerted by the gas pressure above the solid mixture on its transform-
ation rate;

8) the possibility of describing the reaction rate in mixtures of

crystalline solids by the diffusion-kinetics equation derived by Yander from a conception of these reactions as taking place strictly in the solid phase.

The premises set forth above, which form the basis of the Tammann-Khedval doctrine of solid-phase processes, were, in their time, of great assistance in the study of reactions between solids. The Tammann-Khedval theory [215] and the results of their work in this field have been an important stage in the development of our knowledge of crystalline-mixture reactions and served competently as a basis for further research into them.

Vagner [216, 217], Yost [218], Khyutting [204], Yander [219-222], Yagich [223, 224] and other investigators [see, for example, 225 and 226] essentially supplimented and developed certain of the premises of the Tammann-Khedval theory.

On the basis of the work done by these investigators, it was the custom for a long time to extend the conclusions of Tammann and Khedval (and, later, even those of Yander) concerning the mechanism and qualitative laws of reactions between solids to all chemical reactions in which the initial reagents and the final products were in the crystalline state.

On the other hand, the work of Baykov [227, 228], Balarev [39, 229] and many other investigators, including the authors of the present monograph [57, 120, 230, 231], introduced certain changes and refinements into the initial conceptions of the range of validity of certain propositions of the Tammann-Khedval theory.

The possibility of equilibrium being established in the course of reactions between solids in cases of both the formation and nonformation of solid solutions was among the points demonstrated in a number of investigations [219, 232, 233]. It was also established that in many

- 168 -

cases, the temperature of the "onset" (noticeable rate) of a reaction does not coincide with the sintering temperature of the reaction mixture [57, 230, 234]. It was shown that the temperature of noticeable reaction between certain salts and oxides is determined by the nature (dissociation vapor pressure) of the salt [235-237]. Finally, the important part taken by gaseous and liquid phases in many reactions that take place on heating of mixtures of crystalline solids was revealed [120, 137, 227, 228, 230, 238-242].* In this connection, it will be advisable to devote brief consideration to the justification for the propositions of Tammann and Khedval that were presented above.

Let us first stress again the following circumstance, which is frequently overlooked: in any case, there is sufficient evidence for regarding a process as strictly solid-phase if simultaneous absence of significant participation of liquid and gaseous phases has been established in the mechanism of this process.

As we know, very many of the investigations of Tammann and Khedval were concerned with reactions between barium and strontium oxides and various reagents: Balarev [39, 229, 235] at one time drew attention to the possibility of H_2O being contained in these oxides and the hydrates melting in the experiments of Tammann and Khedval. Many years ago, this objection of Balarev was confirmed experimentally by the exact researches of Yagich, who established that it is practically impossible to free barium and stontium oxides from their water contents by ordinary methods [223].

To confirm the second of the arguments presented above in connection with the progress of reactions at temperatures lower than that at which the liquid phase appears in the system, Tammann carried out a special investigation. He compared the temperature at which the liquid phase appears in mixtures of certain oxides with the temperature of the

reaction between them. Here, the temperature at which the liquid phase appeared was judged from the sharp drop in the resistivity of the system that it produced.

TABLE 14

Temperature of "Onset" of Reaction Between Oxides, Spontaneous Heating of Oxide Mixtures, and Sharp Drop in Resistivity, According to Tammann

1 Реагенты	2 Температура в град.		
	3 начала реакции t_1	максимальная, достигаемая в результате 4 разогрева t_2	резкого уменьшения электросопротивления 5 системы t_3
CuO + MoO₃	615	700	250—340
CuO + WO₃	600	800	250—350
FeO + MoO₃	320	580	250—370*
FeO + WO₃	260	800	250—380
BaO + MoO₃	290	580	290—350
BaO + WO₃	300	550	300—360
CaO + WO₃	580	950	630—830
PbO + WO₃	480	700	610—800
MgO + MoO₃	425	650	620—850
MgO + WO₃	300	600	650—840
CaO + MoO₃	425	680	655—830
PbO + MoO₃	460	700	670—820

*Averaging 310°.

1) Reagents; 2) temperature in degrees; 3) begining of reaction, t_1; 4) maximum attained as a result of heating, t_2; 5) sharp drop in system resistivity, t_3.

In all of the cases that Tammann studied in this connection, the reaction mixture was heated spontaneously by the heat of the reaction. On the basis of the data that he obtained, Tammann concluded that since the temperature t_1 at which the reaction begins is in no way related to the temperature t_3 at which the liquid phase appears in the systems, then the latter is not an essential factor in the reactions of crystalline solids and that these processes are solid-phase (Table 14).

It should be noted in this connection that in the first two cases listed in the table (CuO + MoO_3 and CuO + WO_3), the reaction begins after the liquid phase has appeared in the system; in the next four cases, the reaction-onset temperature coincides with the temperature

at which the liquid phase appears. Thus, half of the results listed above are in disagreement, even at first glance, with the conclusion drawn at the time from the tabulated data. In almost all cases (with one exception) $t_2 > t_3$, i.e., the reactions studied actually took place at a temperature t_2 exceeding the temperature t_3 at which the liquid phase appears in the system, even though the start of the reaction was associated with a $t_1 < t_3$. Finally, and this is particularly important molybdenum oxide and tungsten oxide, which were used as reagents in studying the reactions listed in Table 14, are capable of sublimating under the temperature conditions at which Tammann observed the progress of these reactions [243-245]. Thus the data of Table 14 do not confirm the idea that the reactions listed there are strictly solid-phase in nature.

With his third argument, Tammann intended to show that the premise that the material melts in a process of this type as a result of the temperature increase due to the heat of reaction inevitably results in a logical impasse. Tammann stated that liberation of this heat would require preliminary heating of the reagents.

In actuality, escape from this impasse is quite simple. It consists in acknowledging the basic possibility of direct reaction between solids in the process of their transformation, but not necessarily their (quantitatively) preferential importance. If the reaction is exothermic all that liberation of the heat requires is that as small a number as you please of solid particles of the initial reagents be reacted with one another. Obviously, the amount of this heat may be adequate to raise the mixture temperature locally to the melting point of at least one of the reagents (or a eutectic) and convert a certain very small quantity of it to the liquid phase. Then this quantity of reagent, entering the liquid state, reacts intensively with the second reagent,

and, reacts intensively with the second reagent, and this results in further evolution of reaction heat and melting of a new amount of the first reagent and so forth. Here, as we noted above, the reaction goes preferentially through the liquid phase.

This is the situation with the first three arguments, the object of which was to refute the essential importance of the liquid phase in the reaction mechanism for reactions taking place when crystalline mixtures are heated.

The fourth of the arguments of Tammann presented above has as its purpose to show the lack of justification for ascribing any essential role in the mechanism of these reactions to the gaseous phase. It is important to note in this connection that, all other conditions the same, the rate of dissociation or sublimation of a solid is proportional to the difference between its equilibrium dissociation or sublimation vapor pressure and the actual pressure in the gaseous medium of this solid. The "actual vapor pressure" is naturally lower in the presence of an agent that binds a substance entering the gaseous phase chemically into the solid product. In actuality, this drop in the "actual vapor pressure" and corresponding increase in the rate of the process under the conditions being considered is determined by the difference between the equilibrium vapor pressures of this substance over two crystalline phases: the initial phase and the final phase for the process in question. Consequently, the progress of the reaction with a noticeable or relatively high rate at the temperatures at which dissociation or sublimation of a reagent taken separately is unnoticeable or proceeds with a relatively low rate cannot serve as a basis for negating the importance of the gaseous phase in this process.

Usually, the following data are presented to confirm the fifth of the arguments listed above (Table 15).

TABLE 15

Temperature of Noticeable Rate of Reaction Between Certain Oxides and Sulfates, According to Tammann and Khedval

1 Оксиды	2 Температура "начала" реакции (в град.) с сульфатом					
	3 стронция	4 кальция	5 магния	6 кобальта	7 цинка	8 меди
BaO	372	370	369	326	341	345
SrO	—	451	441	431	424	418
CaO	—	—	540	533	520	516
MgO	—	—	—	592	630	—

1) Oxides; 2) temperature of reaction "onset" (in degrees) with sulfate of; 3) strontium; 4) calcium; 5) magnesium; 6) cobalt; 7) zinc; 8) copper.

On the basis of these and certain other (similar) data, Tammann and Khedval asserted that since the temperature of the reaction is in no way related to the type of salt reacting with the oxide in question, the dissociation vapor pressure and, in general, the dissociation of the salt do not represent factors that are in any way significant in these reactions. The reaction is governed by the vibrations of the oxide lattice elements and is strictly solid-phase.

It should be noted in this connection that data concerning the reaction of salts with CaO and MgO do not, even on first inspection, support such a conclusion, since the temperatures of the reactions between each of these oxides and the various salts differ widely. More recent investigations [236, 237] have shown that the difference between the noticeable-reaction temperatures for the various sulfates with a given oxide may be reckoned in tens and hundreds of degrees. Thus, the "temperatures of marked reaction rate" between MgO and $MnSO_4$, $ZnSO_4$ and $Fe_2(SO_4)_3$ are, respectively, 660, 575, 550 and 539; corresponding temperatures for CaO $MgSO_4$, $MnSO_4$, $FeSO_4$, $ZnSO_4$, $CuSO_4$, $Fe_2(SO_4)$ and Ag_2SO_4, are, respectively, 700, 610, 584, 540, 520, 444, 420°, etc. A pattern that is, at first glance, more or less surprising is

obtained for reactions of BaO and SrO with various salts. Here, however, it must be remembered that it is possible for a liquid phase to appear due to melting of $Ba(OH)_2$ and $Sr(OH)_2$ or eutectic mixtures of these substances with others. It is known that the melting point of $Ba(OH)_2$ is about $387°$, while that of $Sr(OH)_2$ is about $495°$; mixtures of these substances with others may, of course, melt at lower temperatures.

The sixth argument of Tammann and Khedval had as its intention to support the proposition formulated in their fourth argument. The matter is not as simple as the reaction between the salt and the oxide taking place under the temperature conditions at which dissociation of the salt taken alone proceeds extremely slowly, as assumed by Khedval [210]: there is no type of relationship between the temperature at which the oxide reacts with the salt and the temperature of the later's noticeable dissociation rate.

Khedval applied the term "temperature of onset of dissociation at noticeable rate" of, e.g., a sulfate, to the temperature at which he observed that a barium nitrate solution trapped, in a certain interval of time, large quantities of SO_3 in a medium of inert gas passed over the heated sulfate. However, on comparing the dissociation vapor pressures at the temperature given by Khedval as that of marked decomposition for these sulfates (Table 16), we see at once that Khedval's definition of the "onset of dissociation at noticeable rate" was not sufficiently rigorous; for strontium and barium sulfates, for example, it is observed at a dissociation vapor pressure reckoned in fractions of a millimeter of mercury, while for cobalt and copper sulfates the value is tens of millimeters and for zinc sulfate hundreds of millimeters of mercury.

The values found for Khedval for temperatures of marked decompos-

ition of the salts apparently depends on his experimental conditions, which were not always uniform. For this reason, the absence of a link between these values and those obtained on the basis of similar determinations of the temperatures of marked rate of reaction of the salts

TABLE 16

Temperature of Marked Decomposition of Pure Sulfates According to Khedval and Their Dissociation Vapor Pressures at This Temperature

1 Сульфат	2 Температура заметного разложения сульфата t	3 Упругость диссоциации сульфата при температуре t в мм рт. ст.*
CaSO₄	660	26
CaSO₄	740	15
ZnSO₄	830	350
MgSO₄	940	2
CaSO₄	1000	~1
SrSO₄	1130	<1
BaSO₄	1300	<1

*According to Vanyakov (see [246]), Mostovich [247] and others [248].

1) Sulfate; 2) temperature of marked decomposition of sulfate; 3) dissociation vapor pressure of sulfate at temperature t in mm Hg.*

with oxides does not form an adequate basis for inferences as to its mechanism.

Also inadequate for such inferences is the establishment of a weak dependence of the rates of certain reactions between solids on the gas pressure over them.

The view is widely held that the rate of reaction between solids with participation of a gaseous phase (which appears, for example, as a result of dissociation), must be proportional to the gas pressure above these materials. However, this standpoint cannot be given a rigorous theoretical justification.

If the process consists, for example, of a dissociation reaction of one of the components in the initial mixture

$$T_1 \rightleftarrows T_2 + Gas$$
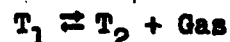
and a reaction of the gas that has been liberated with the second com-

ponent of the mixture with formation of a solid product:

$$Gas + T_3 \leftrightarrows T_4,$$
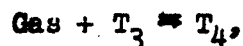
the change in gas pressure in the system may shift both the equilibrium and the rates of these reactions in opposite directions.

It is clear from this that in the general case, we may not speak of any direct or indirect proportionality of the over-all process rate with participation of a gaseous phase to the gas pressure. Under real conditions, depending on the nature of the limiting stage (the limiting "elementary" process), of the reaction and the factors determining its rate, the latter may change slightly in either direction as the pressure changes in a given direction, and this change may be virtually imperceptible.

The question as to the mechanism of the process cannot be definitely resolved even by establishing the validity of one diffusion-kinetics equation or another: in principle, the change of the rate of the process limited by diffusion may be described by an equation of diffusion kinetics (in particular, by the Yander equation in a definite stage of the process) irrespective of the physical state of the diffusing substance - solid, liquid or gaseous. It is known [249] that the equation

$$x = K\sqrt{\tau},$$

(where x is the thickness of the layer of material, K is a constant and τ is time), which is analogous to the Yander equation, is valid even for simple filtration of a liquid or gas through the pores in the layer of solid material being grown in this process.

The above analysis of Tammann and Khedval's reasoning, the basic points of which appeared in the literature of the day [57, 230, 234, 236], and the numerous experimental data concerning the reactions that take place when the crystalline mixtures are heated, lead us to infer

limited validity of certain premises of the Tammann-Khedval theory.

It does not, of course, follow from this that chemical reaction processes between the grains of crystalline solids cannot take place or are not actually encountered. The point is that only some of the real processes that take place in mixtures of crystalline solids when they are heated can be classified as strictly solid-phase.

Many of the processes to which investigators have occasionally attempted to extend the Tammann-Khedval theory actually failed to conform to it, partly because of the inadequate rigor of some of its premises and partly (chiefly) because these processes actually take place with participation of gases and liquid phases.

These processes do, however, belong to the chemistry of solids to the extent that it is actually concerned with study of reactions companied by the widest imaginable variety of physicochemical changes to the initial mixtures of crystalline reagents.

* * *

Conceptions of the mechanism of reactions taking place when crystalline solids are heated were developed considerably and rendered concrete as a result of the studies of Vagner.

In the nineteen-thirties, Vagner and Schottke developed a thermodynamic theory of solids that takes lattice distortions and impurities into account [250, 251]. Subsequent studies of Vagner [252, 253] devoted to the theory of diffusion in solids and the mechanism of new formations in them are based on this theory.

The conceptions formulated and justified in these studies were primarily concerned with the process of metal oxidation at high temperatures, but they were subsequently used successfully to account for many diffusion processes in salts, silicates, and other substances.

According to Vagner, diffusion and, consequently, reactions in

- 177 -

solids are effected chiefly by the mobility of the ions and electrons, which is governed by the nonequilibrium state of the lattice. There is no diffusion through pores and along grain boundaries, and the rate of displacement of electrically neutral molecules and atoms is negligibly small. Different lattice ions migrate at different rates inside the solid; in particular, the mobility of anions is negligibly small in the overwhelming majority of cases as compared with the mobility of cations, so that diffusion and, accordingly, reactions in solids are most frequently effected by cation migration. Here, diffusion of certain (like) cations may occur in one direction, or we may have counterdiffusion of unlike cations, e.g., magnesium ions in one direction and aluminum ions in the other, opposite direction. In the latter case, both the charges and the rates of displacement of the unlike ions diffusing counter to one another may differ.

Here, just as in the case of unidirectional motion of ions, the electrical neutrality of the body is retained by movement of electrons. Thus, motion of each Mg^{2+} ion in a certain direction, which is not compensated by countermigration of a cation, corresponds to the displacement of two electrons in the opposite direction. The motion of the ions and electrons is accomplished by substitution of ionic and electron vacancies, respectively.

Naturally, the mobilities of unlike ions in a system cannot, in principle, be strictly identical. Thus, the mobilities of silver and copper ions, with whose motion the reaction

$$AgI + CuI \rightarrow (AgCu)I$$
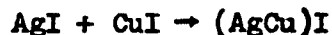
is associated, differ by approximately 50%.

However, in the case of such a mobility difference in the different ions in the system, there arises a diffusion potential that regulates the rate of migration. Here, the migration rate of the more

mobile ions diminishes, while that of the less mobile ions is increased.
As a result, we may speak of some average, approximately uniform rate
of migration of the unlike ions. The average rate of ion and electron
displacement and the rate of the entire reaction in the crystalline
phases, which it determines, can be computed following Vagner, on the
basis of the electron and ion mobilities and the transfer numbers.

Obviously, directional diffusion of ions is possible only in an
electric field or when there is a chemical-potential gradient due to
the presence of a concentration gradient in the system. In the absence
of an electrical or chemical potential, the ions migrate in a disorder-
ed fashion, equally, on the average, in all directions, in much the
same way as particles in Brownian movement in colloidal solutions.

Vagner confirmed his reasoning experimentally for a number of
systems; they agree with the experimental data of Tubandt [254-256]
and certain other investigators.

Using a special apparatus (Fig. 41), Vagner [252] demonstrated the
mechanism by which silver reacts with sulfur. In this apparatus, a sil-
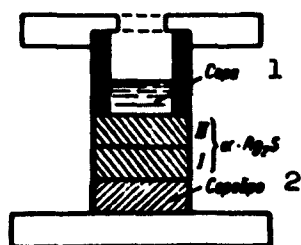
Fig. 41. Diagram
of Vagner's exper-
imental apparatus.
1) Sulfur; 2) sil-
ver.

ver plate was isolated from the molten sulfur
by two identical layers of α-Ag_2S. It was es-
tablished that when the entire system was heat-
ed, e.g., to a temperature above 220°, for one
hour, the weight of the silver diminished by
108 mg, while layer I of Ag_2S increased in
weight by 2 mg and layer II gained 126 mg.
The stoichiometric weight of Ag_2S as computed
assuming complete reaction of all the silver
lost by the metallic plate with sulfur should be 124 mg.

Thus, it was shown that the reaction product forms only in layer
II and that the reaction actually takes place at the $(Ag_2S)_{II}$/S phase

- 179 -

boundary, i.e., at the boundary between the liquid sulfur and layer II of Ag_2S. This means that the silver is transferred through the silver-sulfide layers to the interphase between the (Ag_2S) and the sulfur, while the sulfur does not pass through them. Vagner cccounted for the mechanism of mass transfer in the reaction described by referring to these data and the fact that the conductivity of Ag_2S at the temperatures studied is mixed and is accomplished by simultaneous transfer of ions and electrons. As a result of diffusion in the Ag_2S layers, a concentration gradient of excess Ag^+ ions is established and, as is required for conservation of electrical neutrality, migration of electrons takes place. At the contact boundary between the Ag_2S and the sulfur, the electrons convert sulfur atoms adsorbed onto the Ag_2S surface into ions, which then occupy the corresponding positions in the anion lattice. Reaching the interface, the Ag^+ ions occupy the places of newly created holes in the cation lattice. It is for this reason that the Ag_2S/S interface displaces toward the sulfur as the reaction proceeds. Diffusion of Ag^+ through the Ag_2S is the process that limits the rate at which this reaction proceeds.

Tubandt [255, 256] showed that, for example, in silver halides, only the Ag^+ ions are, for practical purposes, mobile.

The press-cylinder method proposed by Tubandt made it possible to connect the kinetics of certain reactions with the physical characterization of the ions forming the initial reagents.

It was established that in the formation, for example, of spinels by the reaction

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$
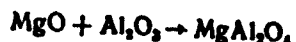
mass transfer is effected by the small Mg^{2+} (0.74A) and Al^{3+} (0.57 A) ions, while the larger oxygen ions (1.36A) remain in their positions.

On this basis, the process may be represented by the following

scheme:

	MgO	$MgAl_2O_4$	Al_2O_3
1 Ионная диффузия		$3Mg^{2+} \rightarrow$ $\leftarrow 2Al^{3+}$	
2 Реакция на границах фаз	$4MgO$ $-3Mg^{2+}$ $+2Al^{3+}$	$4Al_2O_3$ $-2Al^{3+}$ $+3Mg^{2+}$	
3 Продукт:	$MgAl_2O_4$	$3MgAl_2O_4$	

1) Ionic diffusion; 2) reaction at phase boundaries; 3) product.

According to Vagner, this scheme is in full agreement with data on the structure of the spinel lattice, which consists of an ordered oxygen framework and cations with a distribution that is somewhat disordered [257, 258].

Certain reactions in silicate systems may be represented in a similar manner, e.g.:

$$MgO + MgSiO_3 \rightarrow Mg_2SiO_4.$$

In this case, we proceed from the assumption that the diffusing ions are Mg^{2+} and Si^{4+}:

	MgO	$3MgO \cdot SiO_2$	$MgO \cdot SiO_2$
1 Ионная диффузия		$2Mg^{2+} \rightarrow$ $\leftarrow Si^{4+}$	
2 Реакция на границах фаз	$4MgO$ $-2Mg^{2+}$ $+Si^{4+}$	$4MgSiO_3$ $-Si^{4+}$ $+2Mg^{2+}$	
3 Продукт:	$2MgO \cdot SiO_2$	$3(2MgO \cdot SiO_2)$	

1) Ionic diffusion; 2) reaction at phase boundaries; 3) product.

The scheme of the reaction between silver and mercury iodides, as based on the ionic-diffusion conception, reduces to the following:

	AgJ	Ag₂HgJ₄	HgJ₂
1 Ионная диффузия		2 Ag+→ ←Hg²+	
2 Реакция на границах фаз	4 AgJ −2 Ag²+ +Hg²+		2 HgJ₂ −Hg²+ +2 Ag+
3 Продукт:	Ag₂HgJ₄		Ag₂HgJ₄

1) Ionic diffusion; 2) reaction at phase bound-
aries; 3) product. J = iodine.

When the process is effected in accordance with this scheme, the
low-mobility iodine ions remain in position for all practical purposes.

The scheme of the process in which mixed (AgCu)I crystals are
formed from silver and copper iodides is just as simple.

The differing probabilities that ions of different sizes will mi-
grate is a familiar fact in crystal chemistry and the theory of solids,
and one which was briefly touched upon above. Here, it should be stress-
ed that in an ordered lattice, migration of even relatively small ions
that do not possess large charges (for example, Al^{3+} and Si^{4+}) is high-
ly improbable.

In certain cases, e.g., in reactions with carbonates, when migra-
tion of C^{4+} ions represents a highly improbable phenomenon, displace-
ment of oxygen ions in the lattice is regarded as possible.

It is important to note that the Vagner theory, which, in its day,
prompted numerous objections, has turned out to be quite fruitful: it
makes it possible to account for certain diffusion and chemical pro-
cesses in solids and to establish, for example, a relationship between
the diffusion of ions and ionic conductivity (a detailed expression of
the problems concerned here was given by Khaufe [259, 260].

However, as follows from the Frenkel' theory [44, 45] and is in-
dicated by exact investigations using the tagged-atom method [223, 261],

the actual pattern of the diffusion process accompanying a reaction in a solid mixture does not necessarily correspond to the Vagner conception and does so in far from all cases. In many cases, we deal with diffusion of uncharged particles - atoms and molecules.

§3. ORIGIN AND GROWTH OF SEEDS OF NEW PHASE. ROLE OF INTERPHASE SUR-
FACE

It has been established by investigation of various processes in which new phases form that an important and frequently observable stage in many of them (including certain reactions in solids) is the appearance and growth of seeds of the crystalline product.

This stage has been observed in thermal-decomposition reactions of many solids, such as crystal hydrates [262-264], oxalates [265, 266], barium azide [266, 267], ammonium bichromate [268] and the like. Reactions of this type incorporate processes in which initial reaction centers are formed, subsequent development of stable nuclei of the product from these, and three-dimensional growth of the latter with formation of a boundary between the old and the new phases.

In the presence of the [boundary], the process in which seeds of the new phase originate is localized preferentially or even completely at this boundary.

This proposition, which is difficult to prove experimentally by any form of direct measurement, has been given numerous indirect and quite convincing confirmations. These include data on the kinetics of certain reactions.

The fact is that acknowledging localization of the process at the interphase surface is equivalent to acknowledging its autocatalytic nature; it has been established experimentally by various authors [263-270] for many cases.

An interesting method for demonstrating the catalysis of certain
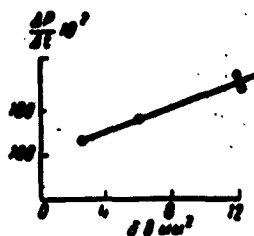
Fig. 42. Maximum thermal-decomposition rate of mercury oxalate as a function of area of preparation previously bombarded by electrons at a temperature of 218°. 1) δ in mm^2.
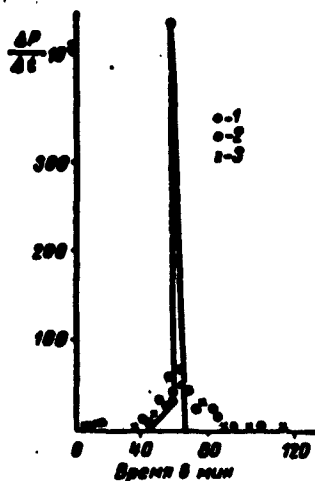

Fig. 43. Thermal-decomposition of silver oxalate. Kinetics of process at 120°. 1) Unilluminated specimen; 2) illuminated unrubbed specimen; 3) illuminated rubbed specimen. $\Delta P/\Delta t$ in mm Hg/min. A) Time in minutes.

reactions by their solid products was employed by Osinovik [266]. Studying the thermal-decomposition reactions of certain compounds, he showed that preliminary creation of an initial-substance/product interphase surface by, for example, partial illumination of silver-oxalate preparations and bombardment of barium azide and mercury oxalate preparations with monoenergetic electrons accelerates their thermal decomposition considerably (Fig. 42). As was shown by Osinovik, breakdown of the phase boundary between the initial substance and the reaction product by, for example, mechanical rubbing of a partially illuminated silver oxalate preparation, results in a decrease in the rate of thermal decomposition of this preparation (Fig. 43).

In both the formation and the disappearance of a crystalline phase, the migration of the particles forming it does not take place in a statistically random fashion, but in definite directions, which depend on the crystallographic form of the initial phase.

As we know, the growth of a heteropolar crystal from a vapor or solution takes place by deposition of particles first at the points or on the edges of the regular crystal, and then by successive laying-on of particles around a row of elements that have already been secured. This procedure is re-

- 184 -

peated in the growth of each successive layer of the crystal. Here, the geometrical complex that arises is similar, as shown in Fig. 44, to the initial complex.

If the planes of the lattice shown in Fig. 44 are in contact with a supersaturated solution of the substance of which the lattice is constructed, a new layer of the lattice will be arranged in accordance with Figure a. The difficulty and rate of formation and development of the various geometrical complexes of the crystal vary, and this makes it anisotropic (page 11).

●-1; ○-2; ✦-3; ◉-4
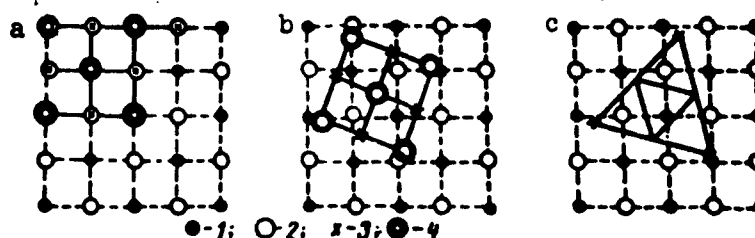
Fig. 44. Probable (a) and improbable (b and c) arrangement of geometrical complexes of ions separated out during crystallization of substance on (001) face of NaCl-type lattice. 1) First-layer cations; 2) first-layer anions; 3) second-layer cations; 4) second-layer anions.

Such is the tentative scheme of the elementary crystallization process. It is also the actual process for other more complex cases of crystallization, including crystallization from vapor and from the melt, crystallization accompanying the decomposition of solids, reduction of metals from the oxides, formation of oxide, halide, sulfide and other films on metals, polymorphic transformations (pages 145-156), and so forth. The unfolding of a crystallization process in accordance with the orientational scheme may be illustrated by reference to the example of formation of the oxide γ-Fe_2O_3 on pure (Armco) iron.

According to Dankov [271, 272] and Nel'son [273], the (111) plane in the iron lattice is parallel to the (210) plane in the lattice of
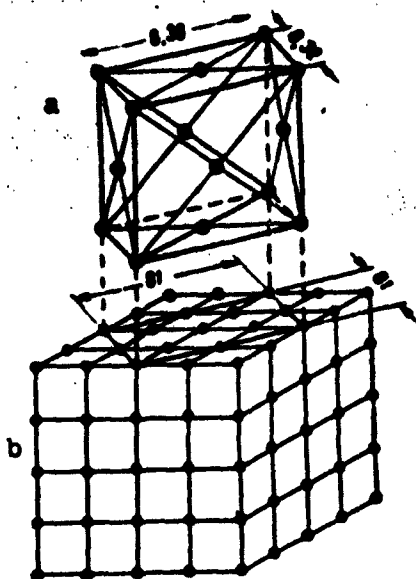
Fig. 45. Correspondence between crystal lattices of α-iron (a) and γ-Fe_2O_3 (b).

Only atoms on the surface of the (001, 010, 100) faces are shown in the iron lattice; only the superficial iron atoms are shown in the elementary γ-Fe_2O_3 cell.

the oxide γ-Fe_2O_3 formed on the surface of iron. Here, these lattices are conjugated with one another by planes of cubes whose sides are turned through a 45° angle with respect to one another (Fig. 45). The dimensions of the limited-similarity geometrical complexes through which these lattices are conjugated differ from one another (see Fig. 45) by approximately 2.6%. All of this is in agreement with electron diffraction data obtained in oxidation of iron [271-273] and with observations made during reduction of Fe_3O_4 [274].

On the basis of theoretical considerations and voluminous experimental data similar to those presented above, Dankov [275, 276] formulated, in his time, the important principle of orientational and dimensional correspondence between crystalline structures, which determines the direction of chemical transformations at the boundary between two phases. According to this principle, the chemical transformation at the surface of the solid develops in such a way that the configuration of the atoms of the initial solid phase will be retained (or almost retained) in the new solid phase as well. The new-phase lattice that arises in this crystallization process is conjugated with the crystal lattice of the initial phase by similar crystal planes whose parameters differ from one another only slightly.

In accordance with this principle, the emergence of a new crys-

talline phase at the boundary with the existing phase during thermal decomposition of a solid takes place with the formation of a forced, unstable crystalline structure in which the atoms are arranged in a definite correspondence with the positions of the same atoms in the initial lattice of the substance. This unstable structure then goes over into the normal structure that is stable under the conditions involved.

It should be noted that in certain cases, the process of new-phase formation may take place independently of the orienting forces of the initial phase. Here, the seeds of the new phase acquire a random orientation with respect to the initial crystalline surface and there is no orientation correspondence. Strictly speaking, the phase transformation at the surface of the solid goes in the direction of formation of a new crystal lattice that is in orientational and dimensional correspondence with the crystal lattice of the initial surface in cases where the deformation energy E of the two-dimensional lattice of the new phase is smaller than the work of formation A of the seed. On the other hand, if $E > A$, the process goes in the direction that does not depend on the structure of the initial-phase surface [276].

In connection with the above statements concerning the role of the interphase surface, it will be advisable to touch upon the possibility of accelerating the reaction by addition of its product to the initial substance. In many cases, attempts at such acceleration produce no effects, a circumstance that may be accounted for on the basis of the orientational-correspondence principle.

The product introduced from without may not be related to the initial substance energetically and sterically to the same degree as the product that is formed in the reaction process. Energetically and structurally, these reaction products are not identical. Naturally, the

product introduced from without cannot have the same effect on the re-
action as the emerging primary crystalline phase, whose structural ele-
ments are in definite spatial crystalline correspondence with the
structural elements of the initial phase [266].

§4. PART TAKEN BY GASEOUS AND LIQUID PHASES

Participation of liquid and gaseous phases in reactions between
solids has an important influence on the conditions of the process, and
chiefly on the size of the reaction-surface area between the reagents.

If the process is taking place in the presence of a gas or liquid,
they will wash the grains, so that the area of the reaction surface
will be equal or closely similar to the grain area of one of the re-
agents.

If the process is taking place by direct interaction between
solid particles, the size of the reaction-surface area may be of a
totally different order. With the usual grain sizes in the real granu-
lar masses (1 to 10^{-3} cm), the average distance between neighboring
grains (page 46ff), which is reckoned in millimeters or microns, is 10^5
to 10^7 times the effective radii of the atomic and other forces linking
the structural elements of the crystal lattice, which are reckoned in
angstroms. When the part taken by surface diffusion in such masses is
insignificant, their reaction surface comes to only 10^{-7} to 10^{-4} of the
total grain area. Under these conditions, the area of chemical reac-
tion, which is effected by direct contact between solid particles, is
smaller by a factor of 10^4 to 10^7 (normally about 10^6) than in a re-
action effected through a gaseous or liquid phase. The value of the
direct-intergranular-contact area for a grain size $R = 1$ to 10^{-3} cm
may be reckoned as being of the order of 10^{-4} to 10^{-6} cm^2 per 1 cm^3 of
reacting mass (see Table 10).

For a reaction to proceed by direct interaction between granules

of the crystalline reagents, mass transfer of at least one of them through a solid layer of product to particles of the other is necessary. In cases where a dense layer of product is formed, mass transfer takes place by internal diffusion. As we know, the values of the diffusion coefficient D of solid into solid lie in the range from 10^{-4} to 10^{-12} cm^2/sec [88, 89], while the specific gravity of crystalline solids (in g/cm^3) and the motive force of the process (expressed in dimensionless form) are reckoned in units.

If we take these data into account, we may conclude on the basis of a simple calculation that when surface diffusion takes a negligible role, the extent of conversion of solids after 1 hour, when it is restricted to diffusion by the above mechanism, amounts to 10^{-8} to 1%, depending on the values of R in cm and D in cm^2/sec.

However, the actual rate of many of the reactions that take place when mixtures of solids are heated is at least two orders and, much more often, four orders higher than the rate obtained by a calculation of this type. In industry, practically complete chemical transformation of crystalline mixtures is obtained after 15-20 minutes of heating or less. According to Khedval [210], many of the reactions in solid mixtures that he studied go almost to completion in a few seconds or even fractions of a second.

Under the conditions described, therefore, the theoretical rate of mass transfer through contact zones in a powdered solid is many times smaller than the rate of mass transfer that is frequently observed in actuality when powdered solids react.

It follows from this that in these cases, which are observed frequently in practice, either surface diffusion plays an essential role or mass transfer is effected not through the usual contact zones in the free-poured powder, but preferentially or almost completely by

other paths. In other words, there occurs in these cases either the first or the second of the previously discussed (page 88) variance of diffusion between the grains of a powdered solid. Combinations of these variants are, of course, also possible. On realization of either of them, the entire grain surface of the powder mixture may participate in the mass-transfer process, and this will ensure a high reaction rate.

In principle, the first variant does not require conversion of the reagent to the liquid or gaseous state.

If the second variant is realized, the process leaves the range of conditions restricted by the action of the bonds between the crystal-lattice elements, i.e., it requires that the solid be converted from the crystalline into the liquid or gaseous state.

Indeed, it is sufficient to allow participation of a gaseous or liquid phase in the reaction to account for intensive mass transfer from one reagent to the other during the process of a reaction between crystalline solids.

If, for example, solids A and B react with one another to form a solid product AB according to the scheme

$$A_\tau \rightarrow A_{ra}$$

$$A_{ra} + B_\tau \rightarrow AB_{\tau \bullet}$$
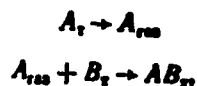
then particles of reagent A, undergoing sublimation in this process, come into contact with the entire surface area of the B grains and, after forming a layer of the product AB on them, diffuse through the latter's entire surface at the rate characteristic of gas diffusion in a solid. In this case, rapid unfolding of the process is ensured by the large areas of the reaction surface and the cross section of the diffusion flow, as well as by the frequently high value of the diffusion coefficient.

In general, many other variants of the reaction mechanism in a solid mixture are possible with participation of gases and liquids. However, the difference between the theoretical and actual reaction rates for any of these variants when there is a rather large average distance between the grains of the initial reagents and a negligibly small contact surface between them is for all practical purposes negligible. It is clear from this that the part taken by gaseous and liquid phases in reactions be ween solids may be highly significant.

An indication of the importance of this role of liquid and gaseous phases in many such reactions is the practically uniform participation of the entire surface area of the grains of the initial mixtures in them. As we know [118, 277 and others], irrespective of the presence and rate of surface diffusion, formation of the product in many such reactions takes place uniformly from beginning to end of the process over the entire surface of the grains of the "coated" reagent, different zones of which nave differing distances from the points of contact with the grains of the other reagent(s). This can be accounted for only by the action of liquid or gaseous substances on the surface of the grains of the "coated" reagent.

Assuming that the role taken by gaseous and liquid phases in the processes of chemical conversion of a solid mixture is of great importance for characterization of their mechanism, we can classify these processes into the following groups:

1) processes of direct reaction between grains of the solids;

2) processes taking place with participation of a gaseous phase;

3) processes taking place with participation of a liquid phase;

4) processes taking place with simultaneous participation of gaseous and liquid phases.

The mechanism of processes in which a solid mixture is converted

with participation of gaseous and liquid phases admits of rather detailed analysis and description [234] taking into account the essential nature and sequence of the basic physicochemical transformations making up these processes. Reactions taking place between solids in the presence of a gaseous phase may represent various combinations of the following simple transformation types:

sublimation of a solid;

dissociation of a solid;

reaction of a solid with a gas to form a solid, i.e., the reverse of the preceding process;

reaction between two gases to form a gas.

Conversions taking place in a solid mixture with participation of a liquid phase may represent various combinations of the following phenomena:

fusion of a solid;

reaction of a solid with a liquid to form a solid;

reaction between liquids to form a solid product that crystallizes from the liquid phase.

Investigation of the so-called solid-phase reactions in which solid, liquid and gaseous phases coexist and participate may be reduced for practical purposes to analysis of the reactions of a liquid with a gas in the presence of a solid and of a solid with a gas in the presence of a liquid.

Let us devote brief consideration to the basic variance of the possible mechanism of solid-mixture reactions taking place with participation of gaseous and liquid phases.

It is convenient to adopt the following designations for this purpose:

A, B, C, etc. — the substances forming the initial or final com-

pounds in the process in question*, e.g., CaO, SO_3, SiO_2, etc.

AB, AC, BD, etc. — combination products of substances A, B, C, etc., e.g., $CaSO_4$, $2CaO \cdot SiO_2$, etc.

The subscripts t, zh, g [solid, liquid, gas] — the physical states of the substances.

To characterize the mechanism of processes taking place with participation of a gaseous phase, it is necessary to ascertain the possible ways in which substances A, B, and so forth, can be converted into the gaseous phase before or during chemical reaction between the initial reagents. Here it must be remembered that a reaction in the presence of a gaseous phase requires only that one of the initial reagents or a substance split off from it be converted to that phase in one form or another; hence the second reagent can be left solid and chemically unchanged until the gas formed from the first component begins to act upon it.

Taking this into consideration, we may reduce the possible states of a reagent in processes taking place with participation of a gaseous phase to the following:

a) the unmodified (in the above sense of the word) state;

b) sublimation, e.g., in accordance with $A_t \rightarrow A_g$;

c) dissociation, for example in accordance with $AB_t \rightarrow A_g + B_t$;

d) conversion into a gaseous product by reaction with a third (gaseous) component present in the system, e.g., in accordance with $A_t + C_g \rightarrow AC_g$.

The reaction between substances that are the result of states b, c and d of one component and a, b and c of another component of the initial mixture may be represented as in Table 17.

The most important of the processes enumerated in the table — I, III, IV, IVa, VI, VIg, VII, VIIa, IX and IXa — take place in ac-

TABLE 17

Schemes of Reactions Taking Place with Participation of Gaseous Phase

1 No. п/п	2 Состояние б первого компонента + состояния а, б, с второго компонента	1 No. п/п	3 Состояние с первого компонента + состояния а, б, с второго компонента	1 No. п/п	4 Состояние d первого компонента + состояния а, б, с второго компонента
I	(ба) $A_\tau + B_\tau \to AB_\tau$	IV	(са) $A_\tau + C_\tau \to AC_\tau$	VII	(da) $AC_\tau + B_\tau \to$ $\to ABC_\tau$
Ia	(ба) $A_\tau + B_\tau \to AB_\tau$	IVa	(са) $A_\tau + C_\tau \to AC_\tau$	VIIa	(da) $AC_\tau + BD_\tau \to$ $\to ABC_\tau + D_\tau$
		IVб	(са) $A_\tau + BD_\tau \to$ $\to ABD_\tau$; $ABD_\tau \to A_\tau +$ $+ AB_\tau + AD_\tau$		
II	(бб) $A_\tau + B_\tau \to AB_\tau$	V	(сб) $A_\tau + C_\tau \to AC_\tau$	VIII	(dб) $AC_\tau + B_\tau \to$ $\to ABC_\tau$
		Va	(сб) $A_\tau + C_\tau \to AC_\tau$		
III	(бс) $A_\tau + C_\tau \to AC_\tau$	VI	(са) $A_\tau + D_\tau \to AD_\tau$	IX	(dс) $AD_\tau + C_\tau \to$ $\to ACD_\tau$
	(бс) $A_\tau + B_\tau \to AB_\tau$	VIa	(са) $A_\tau + D_\tau \to AD_\tau$	IXa	(dс) $AD_\tau + B_\tau \to$ $\to ABD_\tau$
	(ба) $A_\tau + B_\tau \to AB_\tau$	VIб	(са) $A_\tau + C_\tau \to AC_\tau$	IXб	(dс) $AD_\tau + B_\tau \to$ $\to ABD_\tau$
	$a = a$ $\delta = b$ $с = c$ $l = d$	VIa	(са) $A_\tau + C_\tau \to AC_\tau$		
		VIr	(са) $A_\tau + D_\tau \to AD_\tau$; $B_\tau + C_\tau \to BC_\tau$		
		VIл	(са) $A_\tau + D_\tau \to AD_\tau$; $A_\tau + C_\tau \to AC_\tau$		

1) No.; 2) state b of first component + states a, b and c of second component; 3) state c of first component + states a, b and c of second component; 4) state d of first component plus states a, b and c of second component.

cordance with the following schemes:

1 Исходные реагенты	2 Агрегатное состояние	
	3 исходных реагентов	4 конечных продуктов
I	$A_\tau \to A_\tau$ $A_\tau + B_\tau \to AB_\tau$	$T_1 + T_2$	T_3
III	$A_\tau \to A_\tau$ $BC_\tau \to B_\tau + C_\tau$ $A_\tau + C_\tau \to AC_\tau$	$T_1 + T_2$	$T_3 + \Gamma$
IV	$AB_\tau \to A_\tau + B_\tau$ $A_\tau + C_\tau \to AC_\tau$	$T_1 + T_2$	$T_3 + T_4$
IVa	$AB_\tau \to A_\tau + B_\tau$ $A_\tau + C_\tau \to AC_\tau$	$T_1 + T_2$	$T_2 + \Gamma$
VI	$AB_\tau \to A_\tau + B_\tau$ $CD_\tau \to C_\tau + D_\tau$ $A_\tau + D_\tau \to AD_\tau$	$T_1 + T_2$	$T_3 + T_4 + \Gamma$
VIr	$AB_\tau \to A_\tau + B_\tau$ $CD_\tau \to C_\tau + D_\tau$ $A_\tau + D_\tau \to AD_\tau$ $C_\tau + B_\tau \to BC_\tau$	$T_1 + T_2$	$T_3 + T_4$
VII	$A_\tau + C_\tau \to AC_\tau$ $AC_\tau + B_\tau \to ABC_\tau$	$T_1 + T_2(+\Gamma)$	T_3
VIIa	$A_\tau + C_\tau \to AC_\tau$ $AC_\tau + BD_\tau \to ABC_\tau + D_\tau$	$T_1 + T_2(+\Gamma_1)$	$T_3 + \Gamma_2$

	1 Исходные реагенты	2 Агрегатное состояние	
		3 исходных реагентов	4 конечных продуктов
IX	$A_r + D_r \to AD_r$ $BC_r \to B_r + C_r$ $AD_r + C_r \to ACD_r$	$T_1 + T_2 (+\Gamma_3)$	$T_2 + \Gamma_3$
IX$_a$	$A_r + D_r \to AD_r$ $BC_r \to B_r + C_r$ $AD_r + B_r \to ABD_r$	$T_1 + T_2 (+\Gamma_3)$	$T_2 + \Gamma_3$

1) Initial reagents; 2) physical state; 3) initial reagents; 4) final products.

To characterize the mechanism of processes taking place with participation of a liquid phase, we present the possible paths of conversion of the components into the liquid phase in a manner similar to the above. This transition may take place by melting of either the pure reagent or a more or less low-melting mixture formed by two reagents or one of them with the reaction product, or by one of them with an inert substance I present in the initial mixture, and so forth.

The possible states (before the beginning of chemical conversion) of the reagent in reactions between two substances that take place with participation of a liquid phase can be reduced basically to the following:

a) the unmodified physical state;

b) fusion of the pure reagent;

c) fusion of a mixture of reagent 1 plus reagent 2;

d) fusion of a mixture of reagent with product;

e) fusion of a mixture of a reagent with an inert substance;

f) fusion of a mixture of reagent 1, reagent 2 and an inert substance;

g) fusion of a mixture of reagent 1, reagent 2 and the product;

h) fusion of a mixture of a reagent, the product, and an inert substance.

Excluding the states that can be eliminated logically in analyzing

- 195 -

the combined behavior of two reagents, we may compile the following
list of basic variants of the mechanism of such processes:

	1) Исходные реагенты	2) Агрегатное состояние	
		3) исходные реагенты	4) конечные продукты
X	$A_\tau \to A_\text{m}$ $A_\text{m} + B_\tau \to AB_\tau$	$T_s + T_\text{a}$	T_a
Xa	$A_\tau \to A_\text{m}$ $A_\tau + B_\tau \to AB_\tau$ $AB_\tau + B_\tau \to (AB + B)_\text{m}$ $A_\text{m} + B_\text{m} \to AB_\tau$	$T_s + T_\text{a}$	T_a
XI	$A_\tau + B_\tau \to (A + B)_\text{m}$ $A_\text{m} + B_\text{m} \to AB_\tau$	$T_s + T_\text{a}$	T_a
XII	$A_\tau + H_\tau \to (A + H)_\text{m}$ $A_\text{m} + B_\tau \to AB_\tau$	$T_s + T_s(+T_\text{a})$	$T_\text{a}(+T_\text{a})$
XIII	$A_\tau + B_\tau + H_\tau \to (A + B + H)_\text{m}$ $A_\text{m} + B_\text{m} \to AB_\tau$	$T_s + T_s(+T_\text{a})$	$T_\text{a}(+T_\text{a})$
XIV	$A_\tau + B_\tau \to AB_\tau$ $AB_\tau + A_\tau \to (AB + A)_\text{m}$ $A_\text{m} + B_\tau \to AB_\tau$	$T_s + T_\text{a}$	T_a
XV	$A_\tau + B_\tau \to AB_\tau$ $AB_\tau + A_\tau + B_\tau \to (AB + A + B)_\text{m}$ $A_\text{m} + B_\text{m} \to AB_\tau$	$T_s + T_\text{a}$	T_a
XVI	$A_\tau + B_\tau \to AB_\tau$ $AB_\tau + A_\tau + H_\tau \to (AB + A + H)_\text{m}$ $A_\text{m} + B_\tau \to AB_\tau$	$T_s + T_s(+T_\text{a})$	$T_\text{a}(+T_\text{a})$

1) Initial reagents; 2) physical state; 3)
initial reagents; 4) final products.

It is important to note that in all of the processes of chemical
conversion of solids described above as taking place with participa-
tion of a gaseous phase, we begin with solid reagents and obtain a
solid product. Nevertheless, in some of these processes, a reaction
takes place between the solids and a gas, while in others the solid
as such does not enter into reaction at all with other substances, and
in no such process is there direct interaction between solids.

As concerns the processes of chemical transformation of a solid
mixture that take place with participation of a liquid phase, in none
of them is there any significant reaction between solid and solid, al-
though superficially, on the basis of the physical state of the initial
substances and the final products, these processes again show no dif-
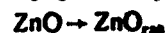ferences from the strictly solid-phase processes in the overwhelming

majority of cases.

It will be helpful to give a brief description of the processes enumerated above and to illustrate some of them with examples.

1. $(A_s \rightarrow A_t; \; A_t + B_s \rightarrow AB_s)$.

In this process, sublimation of solid reagent A takes place first, followed by reaction of gaseous A with solid B.

As examples of this type of process, we may cite, on the basis of experimental data obtained by various authors [223, 278, 279], the reaction between zinc and aluminum oxides to form spinel:

$$ZnO + Al_2O_3 \rightarrow ZnAl_2O_4:$$
$$ZnO \rightarrow ZnO_{газ}$$
$$ZnO_{газ} + Al_2O_3 \rightarrow ZnO \cdot Al_2O_3$$

and the combination of silver iodide with mercuric iodide:

$$HgJ_2 + 2AgJ \rightarrow Ag_2HgJ_4:$$
$$HgJ_2 \rightarrow HgJ_{2\,газ},$$
$$HgJ_{2\,газ} + 2AgJ \rightarrow Ag_2HgJ_4.$$

The process by which silicon monoxide is reduced in formation of silicon carbide from silica and carbon proceeds by the same route [280, 281]:

$$SiO_2 \rightarrow SiO_{газ},$$
$$SiO_{газ} + 2C \rightleftarrows SiC + CO.$$
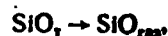
Here, silicon monoxide is formed by dissociation of the dioxide:

$$2SiO_2 \rightleftarrows 2SiO + O_2$$
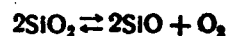
or by the reaction between it and elementary silicon, which is present in liquid form [280, 282 and others] in the reaction zone:

$$SiO_2 + Si \rightleftarrows 2SiO.$$

None of this excludes the possibility of reduction of the silica also by the carbon monoxide formed in the course of the process. Either way, there is actually no direct interaction between solids in the reaction $SiO_2 + 3C \rightleftarrows SiC + 2CO$, even though the initial reagents were

solid.

III. $(A_s \rightarrow A_r;\ BC_s \rightarrow B_s + C_r;\ A_r + C_r \rightarrow AC_s)$.

In this process, as in the preceding process, sublimation of the solid A takes place. The solid BC dissociates and the solid residue (product) C of its dissociation interacts with the gaseous A.

On the basis of data on the volatility of molybdenum oxide [243-245], we may state that, for example, the reaction of MoO_3 with calcium carbonate takes place in this way:

$$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2,$$
$$MoO_{sr} \rightarrow MoO_{srar},$$
$$CaCO_3 \rightarrow CO_2 + CaO,$$
$$MoO_{srar} + CaO \rightarrow CaMoO_4.$$

IV. $(AB_s \rightarrow A_s + B_r;\ A_r + C_s \rightarrow AC_s)$.
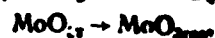
Here, dissociation of one of the components of the initial mixture and bonding of the gas evolved in the process by its second component take place.

We may assume on the basis of the conception of continuous dissociation of salts of oxygen-containing acids (sulfuric, phosphoric, carbonic, and others) and oxides of metals under any temperature conditions that reaction processes between such salts and oxides of metals take place by this route, as, for example,

$$CuSO_4 + PbO \rightarrow CuO + PbSO_4:$$
$$CuSO_4 \rightarrow SO_3 + CuO,$$
$$SO_3 + PbO \rightarrow PbSO_4$$
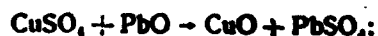
as do reactions between metal oxides and metals, as, for example,

$$CuO + Mg \rightarrow MgO + Cu:$$
$$2CuO \rightarrow O_2 + 2Cu,$$
$$O_2 + 2Mg \rightarrow 2MgO.$$
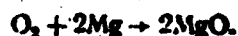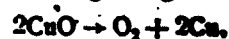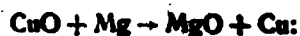
The validity of the last scheme, which represents the mechanism of reaction between a metal oxide and a metal, has been established by a series of investigations conducted by Soviet scientists in the field

of the theory of metallurgical processes [227, 283, 284].

IVa. $(AB_t \rightarrow A_t + B_t;\ A_t + C_t \cdots AC_t)$.

This process differs from the preceding in the formation of a gaseous product AC in the reaction of one of the solid reagents with the gaseous product A_g of dissociation of the other solid reagent.

According to Tammann [285], the processes in which metals are reduced from their oxides by solid carbon, which are highly important for industry, take place preferentially in accordance with this scheme:

$$2\text{MeO} \rightarrow 2\text{Me} + \text{O}_2.$$
$$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$$

or

$$\text{C} + \text{O}_2 \rightarrow \text{CO}_2.$$
$$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}.$$
$$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2.$$
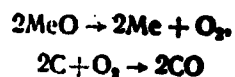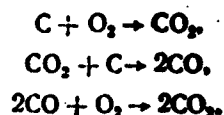
In actuality, the part taken by this scheme in processes in which carbon is used to reduce metallic oxides is quite limited.

IVb. $(ABC \rightarrow A_t + AB_t + AC_t;\ A_t + BD_t \rightarrow ABD_t;$
$ABD_t \rightarrow A_t + AB_t + AD_t)$.
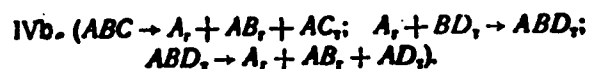
In this case, one of the gaseous dissociation products of the solid ABC (not indicated in Table 17) reacts with solid BD. The product ABD of this reaction dissociates, forming a solid AD and, in much the same way as the dissociating ABC, gaseous A and AB.

One variant of this process is the case in which an initial mixture contains BC — a compound of some of the elements that form its second component ABC — instead of BD.

It may be assumed on the basis of the work done by a number of investigators [236, 237, 248, 286*, 541] that the mechanism by which sulfates react with sulfides corresponds to this scheme.

In the particular case when the initial mixture consists of a sulfate (ABC) and a sulfide (BC) of the same metal, e.g., zinc, the reaction between them
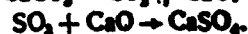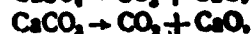
$$3ZnSO_4 + ZnS \rightarrow 4ZnO + 4SO_2$$

reduces to the reactions

$$ZnSO_4 \rightleftarrows ZnO + SO_3$$
$$SO_3 \rightleftarrows SO_2 + \frac{1}{2}O_2,$$
$$2O_3 + ZnS \rightarrow ZnSO_4 \text{ etc.}$$
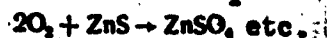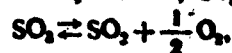
In the general case, oxides of two metals may be present in the solid products of the process.

VI. $(AB_r \rightarrow A_r + B_r; \quad CD_r \rightarrow C_r + D_r; \quad A_r + D_r \rightarrow AD_u).$

Dissociation of the initial components AB and CD and chemical reaction of the gaseous dissociation product of one of these components with the solid dissociation product of the other take place in this process.

The reaction between copper sulfate and calcium carbonate may obviously serve as an example of such a process:

$$CuSO_4 + CaCO_3 \rightarrow CaSO_4 + CuO + CO_2;$$
$$CuSO_4 \rightarrow SO_3 + CuO;$$
$$CaCO_3 \rightarrow CO_2 + CaO,$$
$$SO_3 + CaO \rightarrow CaSO_4.$$

VII. $(A_r + C_r \rightarrow AC_r; \quad AC_r + B_r \rightarrow ABC_r).$

In the present case, one of the components of the solid mixture reacts with the gas C present in the reaction zone with formation of a gaseous product AC, which then reacts with the second component of the initial mixture, forming a solid product.

VIIa. $(A_r + C_r \rightarrow AC_r; \quad AC_r + BD_r \rightarrow ABC_r + D_r).$

Here, on reaction of the gaseous substance AC that has formed as indicated earlier with the solid component BD of the initial mixture, solid and gaseous products are formed.

The processes in which metal oxides are reduced by carbon, for example, $MeO + CO \rightarrow Me + CO_2$, take place in such a manner:

$$C + CO_2 \rightarrow 2CO,$$
$$MeO + CO \rightarrow Me + CO_2$$
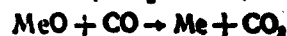
as does reduction of the sulfates of certain metals, e.g.,

$$BaSO_4 + 4C + 2O_2 \rightarrow BaS + 4CO_2:$$
$$2C + O_2 \rightarrow 2CO$$
$$(\quad C + CO_2 \rightarrow 2CO),$$
$$4CO + BaSO_4 \rightarrow 4CO_2 + BaS.$$

IX. $(A_r + D_r \rightarrow AD_r;\quad BC_r \rightarrow B_r + C_r;\quad AD_r + C_r \rightarrow ACD_r).$
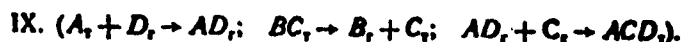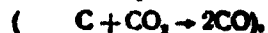
This process differs from the preceding in that the gaseous AD, which has been produced by the same route as AC in process VII, reacts with the solid dissociation product of the second component in the mixture.

Certain processes whose apparent mechanism corresponds to the scheme VIIa may, in actuality, take place in accordance with the above scheme.

X. $(A_r \rightarrow A_x;\quad A_x + B_r \rightarrow AB_r).$

This scheme provides conditions under which one of the components of the initial mixture is melted in the pure state, after which it reacts with the second mixture component.

The reaction of silver with sulfur at temperatures above 113°,[**] i.e., the case in which the sulfur melts: $2Ag + S \rightarrow Ag_2S$, may serve as an example of such a process:

$$S_r \rightarrow S_x,\quad S_x + 2Ag \rightarrow Ag_2S.$$

In this case, the quantity of liquid phase, which is maximal at the start of the reaction, diminishes continuously as it proceeds.

Xa. $[A_r \rightarrow A_x;\quad A_x + B_r \rightarrow AB_r;\quad AB_r + B_r \rightarrow (AB + B)_x;\quad A_x + B_x \rightarrow AB_r].$
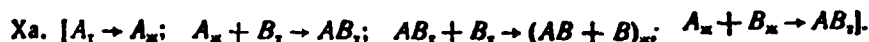
Here we refer to the case in which a product AB formed by scheme I forms with reagent B mixtures that melt under the conditions with which the process is run (at a temperature lower than the melting point of the pure B and AB). On the appearance of the first quantities of the product AB, a quantity of B that corresponds to the composition of such a mixture goes into the liquid phase and reacts with the

liquid A. As the process unfolds, the quantity of B that goes over in-
to the liquid state and reacts with A per unit time increases until
its increase is limited by a deficiency of B or A. On attainment of
certain proportions between the product AB and the reagent B in the
system, corresponding to the composition of the mixture (AB + B) that
melts at the temperature in question, all of reagent B goes over into
the liquid state and from this moment on the quantity of liquid re-
agent B diminishes; this is accompanied by a rapid drop in the rate of
the over-all process.

XI. $[A_r + B_r \rightarrow (A + B)_m; \quad A_m \xrightarrow{} B_m \rightarrow AB_r].$
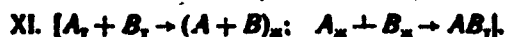
In this case, we have fusion of the mixed initial components A
and B. Here, one of them is always completely melted. The quantity of
the second reagent in the liquid phase at various stages of the pro-
cess and at various process rates depends on the composition of the
mixture that melts at the temperature in question and the proportional
quantities of A and B in the system.

XII. $[A_r + H_r \rightarrow (A + H)_m; \quad A_m \xrightarrow{} B_r \rightarrow AB_r].$
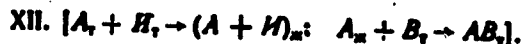
Here, component A of the initial mixture goes over into the
liquid state as a result of its fusion in mixture with component I,
which does not participate in the chemical reaction. Thereafter, the
liquid A reacts with solid B as in scheme X.

The constant-temperature rate of the process at each given point
in time depends on the quantity of liquid reagent A present. The
latter is governed by the composition of the A + I mixture that melts
at the temperature in question and the proportion between the sub-
stances A and I in the system. If the quantity of I is much smaller
than is required to convert all of A to the liquid phase, the quan-
tity of liquid A remains constant during the process until there is
enough A in the system to maintain all of the I in the liquid state.

Here, as A is converted into AB, a corresponding quantity of A goes over into the liquid. Beginning from this point in time, the quantity of liquid A diminishes continuously as the process advances, and this inevitably affects the rate of the reaction.

If the quantity of substance I in the system is adequate to convert all of A into the liquid phase at the very beginning of the process, the rate of the process, which is at first high, drops rapidly in accordance with the continuous reduction in the amount of liquid A in the system from the beginning to the end of the process.

At a temperature below the melting point of substance I, its distribution (like that of reagent A) between the solid and liquid phases at each moment is determined by the prevailing I:A ratio in the system and by the composition of the mixture that melts at this temperature. As the quantity of A diminishes during the process, I may crystallize progressively from the melt; as A → 0, the entire mass of component I becomes solid.

At a temperature of ~500°, the reaction of calcium chloride with barium sulfate in the presence of sodium chloride should take place according to scheme XII.

$$CaCl_2 + BaSO_4 \rightarrow CaSO_4 + BaCl_2.$$

As we know, calcium chloride and sodium chloride form a eutectic that melts at t ~ 500°. The melting points of all other combinations of the initial components of this reaction mixture are at least 500°. As a result, the process may consist preferentially of the following transformations at this temperature during the initial period of the process:

$$CaCl_2 + NaCl_2 \rightarrow (CaCl_2 + NaCl)_m,$$
$$CaCl_m + BaSO_n \rightarrow CaSO_n + BaCl_m.$$
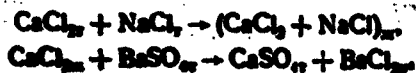
Subsequently, the low-melting mixture of the three chlorides — those of

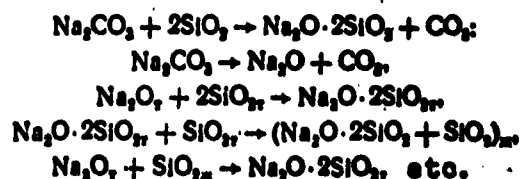calcium, sodium and barium — may go over into the liquid phase.

XIII. $[A_\tau + B_\tau + H_\tau \rightarrow (A + B + H)_{\mu}; \quad A_{\mu} + B_{\mu} \rightarrow AB_\tau]$.

This process is characterized by formation of ternary mixtures
(A + B + I) that are lower-melting than A, B and I taken separately.
As a result, substances A and B go over into the liquid phase and re-
act thereafter in the liquid state.

Since $BaSO_4$ dissolves in liquid calcium chloride, occurrence of
this reaction in the presence of NaCl at temperatures from 500 to 600°
by scheme XIII as well is not excluded.

XIV. $[A_\tau + B_\tau \rightarrow AB_\tau; \quad AB_\tau + A_\tau \rightarrow (AB + A)_{\mu}; \quad A_{\mu} + B_\tau \rightarrow AB_\tau]$.

Here the reaction first takes place between the solid reagents A
and B, yielding a certain quantity of a product AB. The latter forms a
system with A that is lower-melting than A and B. As a result, A goes
into the liquid phase in a quantity corresponding to the composition
of the (AB + A) system that melts at the temperature in question and
to the initial quantity of AB, and thereafter reacts with the solid B.
The technically important reaction between sodium oxide and silicon
dioxide in a mixture of soda with silica takes this path in the tem-
perature range from ~790 to 840°:

$$Na_2CO_3 + 2SiO_2 \rightarrow Na_2O \cdot 2SiO_2 + CO_2;$$
$$Na_2CO_3 \rightarrow Na_2O + CO_2,$$
$$Na_2O_\tau + 2SiO_{2\tau} \rightarrow Na_2O \cdot 2SiO_{2\tau},$$
$$Na_2O \cdot 2SiO_{2\tau} + SiO_{2\tau} \rightarrow (Na_2O \cdot 2SiO_2 + SiO_2)_{\mu},$$
$$Na_2O_\tau + SiO_{2\mu} \rightarrow Na_2O \cdot 2SiO_{2\tau}, \quad \text{etc.}$$

This temperature range is limited at one end by the melting
point of the sodium orthosilicate/silica eutectic (789°) and by that
of the metasilicate/sodium orthosilicate eutectic (837°).

As we know, the pure sodium silicates and silicon dioxide melt
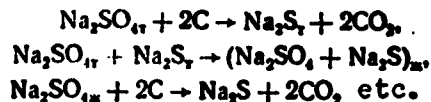at higher temperatures.

The reaction between sodium silicate and carbon

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2,$$
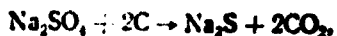
which is of great practical importance and has been studied by Minayev [287], Budnikov and Nekrich [288], Chirkov [289] and other investigators, may, to some extent, take place by a similar route in the temperature range from 710 to 880°.

Since the melting point of Na_2SO_4 is ~880°, that of Na_2S is above 1000°, and that of their eutectic mixture is 740°, all of the sodium sulfate is in the crystalline state in this temperature range before the first Na_2S particles appear. However, as soon as the first Na_2SO_4 particles react with carbon to form Na_2S, transition of the sulfate Na_2SO_4 into the liquid phase begins, and thereafter proceeds with increasing intensity.

The process may be represented by the following scheme:

$$Na_2SO_{4r} + 2C \rightarrow Na_2S_r + 2CO_{2r}$$
$$Na_2SO_{4r} + Na_2S_r \rightarrow (Na_2SO_4 + Na_2S)_m,$$
$$Na_2SO_{4x} + 2C \rightarrow Na_2S + 2CO_2 \text{ etc.}$$

This does not exclude the possibility that the carbon may reduce a large (apparently, the major) part of the sodium sulfate to the sulfide with participation of the gaseous phase [234].

XV. $[A_r + B_r \rightarrow AB_r; \quad AB_r + A_r + B_r \rightarrow (AB + A + B)_{x}; \quad A_x + B_x \rightarrow AB_r]$.

In this process, after a certain quantity of the initial reagents A and B has reacted in the solid state, the three-component system formed by the reagents and the product goes over into the liquid phase. Thereafter, A and B react for the most part in the liquid state, forming more and more of the product AB, which accordingly binds new quantities of A and B into the liquid phase. This goes on until the quantities of A and B in the system are adequate to maintain all of the product AB in the liquid state. The compound AB crystallizes when this moment is reached.

XVI. $|A_7 + B_7 \rightarrow AB_7$; $AB_7 + A_7 + H_7 \rightarrow (AB + A + H)_m$; $A_x + B_7 \rightarrow AB_7|$.

This process differs from the foregoing in that one of the reagents, the product and an inert material present in the initial mixture form a relatively low-melting three-component system.

It will be appropriate here to touch upon yet another "solid-phase" process, even though it does not fit any of schemes I-XVI. We refer to the important industrial reaction used to produce calcium carbide from solid calcium oxide and carbon, which takes place at $1900-2000^\circ$.

The melting point of CaO is 2570°, and that of CaC_2 is 2300°. Even at considerably higher temperatures, the carbon remains in the solid state.

However, according to the data of El [290], which have also been confirmed by other authors, the CaO-CaC_2 system has a compound CaO·CaC_2 with a melting point of 1980° and two eutectics with the compositions 69 and 35% (by weight) of CaC_2 and melting points of 1750 and 1800°, respectively.

Consequently, when this process takes place under industrial conditions (at a temperature of $1900-2000^\circ$), the appearance of the first quantities of calcium carbide is followed by rapid conversion of its oxide into the liquid phase. This may be followed by a reaction between the liquid calcium oxide and the solid carbon (scheme XIV) or, to a certain extent, with its higher oxide, vaporization of the calcium oxide and its reduction in the gaseous phase, some dissociation of calcium oxide and binding by the carbon of the oxygen formed during this process [291].

In all of the processes that we have considered and similar processes, the initial reagents react with one another with participation of the liquid or gaseous phases (or both) decisive.

Such are the basic paths of chemical conversion of a solid mixture taking place with participation of a gaseous or liquid phase. It is neither possible nor necessary here to devote detailed analysis to all of the theoretically conceivable variants of the mechanism of the so-called solid-phase reactions actually taking place with participation of gaseous and liquid phases or, in particular, to concern ourselves with reactions in which solids, gases and liquids coexist and participate simultaneously. This problem is considered in greater detail in earlier published papers [230, 234].

The above exposition touches upon the basic points of this problem and covers the mechanism of reactions having practical significance.

Under real conditions, the mechanism of these reactions may, naturally, be complicated by the formation of multicomponent, relatively low-melting mixtures in the system and the over-all process taking place in several stages, with the appearance of intermediate products, side reactions, solid solutions, temperature changes in the conversion process and other phenomena.

None of this dispenses with the necessity or eliminates the possibility of evaluating the parts taken by gases and liquids in analyzing the mechanism of these reactions (in the complex cases noted, the process can be broken down into a series of component stages for analysis of the mechanism of each of them in isolation).

Here it is important to remember two circumstances:

1) many technically important reactions that take place on heating of a solid mixture are effected with participation of gases or liquids or both simultaneously;

2) the mechanism of these reactions admits of detailed analysis, which ascertains the essential nature, sequence and importance of the basic physicochemical transformations that compose these reactions.

If the part taken by gases and liquids in the mechanism of these reactions is ignored, our conceptions as to the physicochemical relationships controlling these reactions are frequently also found to be erroneous.

Among other things, we frequently encounter in the literature unjustified negations of the possibility of equilibrium in reactions taking place on heating of solid mixtures, in contradiction to the results of Shpring [166] and Yander [219, 220, 243]. In actuality, it is not difficult to conceive of conditions under which such an equilibrium might arise: this might occur in many of the reaction types described above that involve formation of solid solutions, participation of liquid phases, evolution of certain substances into the gaseous phase, and the like.

Obviously, the feasibility of the number of degrees of freedom computed by the phase rule, the validity of the law of effective masses and certain other laws for these reactions, the correctness of considerations concerning their limiting stage and kinetics, and, consequently, the justification for selecting conditions for their practical realization depend on the objectiveness with which we understand the mechanism of the various groups of reactions considered and evaluate the part taken by the gaseous and liquid phases in them.

It is clear from this that in considering the basic problems of solid-state chemistry, studying the theory of the reactions associated with solids, and solving problems in their practical realization, it is necessary to bear in mind the important role taken by gaseous and liquid substances in many such reactions.

§5. SEQUENCE OF CHEMICAL TRANSFORMATIONS

We can consider, in general form, only certain aspects of this problem that are characteristic for a large number of the reactions of

interest to us.*

TABLE 18

Primary Products of Chemical Reactions Between Various Oxides

1 Системы	2 Молекулярные соотношения окислов в соединениях, образующихся в системе	3 Первичный продукт взаимодействия окислов
$MgO - Al_2O_3$	1; 1:6	$MgO \cdot Al_2O_3$
$CaO - Al_2O_3$	3; 5:3; 1; 1:2; 1:6	$CaO \cdot Al_2O_3$
$SrO - Al_2O_3$	3; 2; 1; 1:2; 1:6	$SrO \cdot Al_2O_3$
$BaO - Al_2O_3$	3; 2; 1; 1:6	$BaO \cdot Al_2O_3$
$CaO - Fe_2O_3$	2; 1; 1:2	$2 CaO \cdot Fe_2O_3$
$MgO - SiO_2$	2; 1	$2 MgO \cdot SiO_2$
$CaO - SiO_2$	3; 2; 2:3; 1:2	$2 CaO \cdot SiO_2$
$SrO - SiO_2$	2; 1	$2 SrO \cdot SiO_2$
$BaO - SiO_2$	2; 1; 2:3; 1:2	$2 BaO \cdot SiO_2$
$MgO - TiO_2$	2; 1; 1:2	$MgO \cdot TiO_2$
$CaO - TiO_2$	3:2; 1	$CaO \cdot TiO_2$
$PbO - MoO_3$	2:1	$PbO \cdot MoO_3$
$PbO - WO_3$	2; 1	$PbO \cdot WO_3$

1) System; 2) molecular proportions of oxides in compounds formed in system; 3) primary product of reaction between oxides.

As we know, the direction of a chemical process in a crystalline mixture may not be the same as the direction that it takes in aqueous solution. Thus, the reaction

$$BaCO_3 + Na_2SO_4 \rightleftarrows BaSO_4 + Na_2CO_3$$
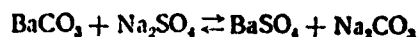
goes to the right in aqueous solution, while it goes in the opposite direction at high temperatures in a crystalline mixture.

It is assumed that the direction of a reaction, which is determined by the solubility product for a solution, depends on the sign of the reaction heat effect in the case of a crystalline mixture.

The direction and probability of a given reaction in a solid mixture are determined more rigorously by calculations based on the general premises of thermodynamics (see Chapter 4).

A distinctive property of many reactions in crystalline mixtures is that they take place in stages: while various compounds may be formed by the reaction between the reagents, the process in which the final product forms passes through a series of stages or steps.

- 209 -

It has been established by the studies of Veyer [118], Yander [219, 220, 243], Berezhnoy [292], Bubenin [293], Toropov [119, 277] and other authors that the sequence in which the intermediate products form does not depend on the proportions between the reagents in the initial mixture. Irrespective of the value of this proportion, the primary reaction product in a given reagent mixture is a definite compound (see, for example, Table 18) that is usually distinguished from the other possible compounds of the system by having the highest crystallization temperature. This compound reacts further with one of the starting components, perhaps with formation of subsequent intermediate products, which sometimes react with the first compound or with one another, and, finally, the target product is formed.

The number of stages may naturally be different for different systems.

It is interesting that even in the simplest binary systems, such as $CaO + SiO_2$, $MgO + SiO_2$, $BaO + SiO_2$, $CaO + Fe_2O_3$, $CaO + Al_2O_3$ and the like, the process passes through a number of stages at constant temperature.

Thus, in the reaction between calcium oxide and silicon dioxide taken in 1:1 proportions, calcium orthosilicate forms first and is subsequently joined by $3CaO \cdot 2SiO_2$. Vigorous formation of the metasilicate $CaO \cdot SiO_2$, the composition of which corresponds to the proportions of the components in the initial mixture (Figs. 46 and 47), begins only in subsequent stages [118, 219, 220, 243].

A somewhat similar pattern is also observed in the reaction of silicon dioxide with magnesium oxide (Fig. 48) and barium oxide (Fig. 49).

According to Bubenin [293], who studied chemical reactions in the $MgO-SiO_2$ system at temperatures from 1100-1170°,

$$MgO \cdot SiO_2 + MgO \rightarrow 2MgO \cdot SiO_2;$$
$$2MgO \cdot SiO_2 + SiO_2 \rightarrow 2(MgO \cdot SiO_2).$$
$$MgO + SiO_2 \rightarrow MgO \cdot SiO_2.$$
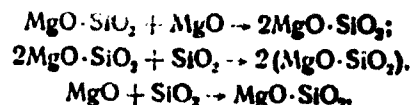
the rate of the first of these reactions is highest. It is for this reason that at the beginning of the process we observe preferential formation of the orthosilicate; the metasilicate, which appears, for example, by the third reaction, is converted almost immediately into $2MgO \cdot SiO_2$.

Only later, as the MgO becomes bound, does the remaining silicon dioxide react with the orthosilicate to form $MgO \cdot SiO_2$.

The primary product of the reaction between calcium oxide and ferric oxide, according to Toropov and Dyuko [277], is bicalcium ferrite. Its reaction with the unreacted ferric oxide then continues with formation of other calcium ferrites.

The mechanism of chemical reactions in multicomponent systems is more complex. Among these, the three-component systems $CaO-Al_2O_3-SiO_2$ and $CaO-MgO-SiO_2$ merit brief consideration. The former is of great importance in the production of Portland cements, slag cements, slag wools and ceramic articles, while the latter is important for refractory production.

Two congruently melting three-component compounds are known in the $CaO-Al_2O_3-SiO_2$ system: helenite $2CaO \cdot Al_2O_3 \cdot SiO_2$ and anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$.

According to the observations of Ginzberg and Lygina [294], the process by which anorthite is synthesized from the oxides at temperatures from 1100 to $1200°$ takes place as follows. First to form as intermediate products are an aluminate of the composition $mCaO \cdot nAl_2O_3$ (12:7), bicalcium silicate $\beta-2CaO \cdot SiO_2$ and calcium metaaluminate and metasilicate
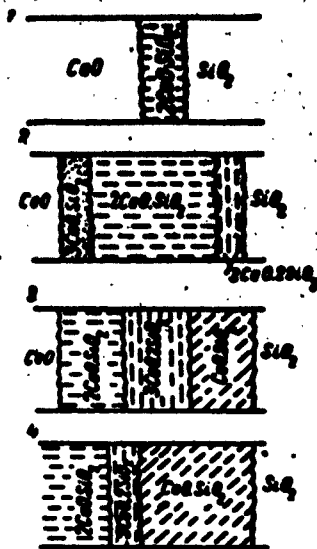
Fig. 46. Basic stages
in process of formation
of monocalcium silicate
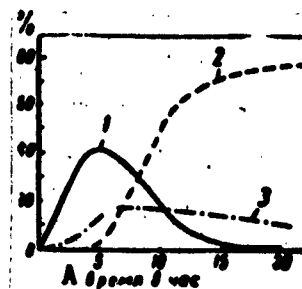in reaction of CaO with
SiO_2.

Fig. 47. Sequence of
formation of compounds
in mixture of 2CaO +
+ SiO_2 at temperature of
$1200°$. 1) Ca_2SiO_4; 2)
$CaSiO_3$; 3) $Ca_3Si_2O_7$.
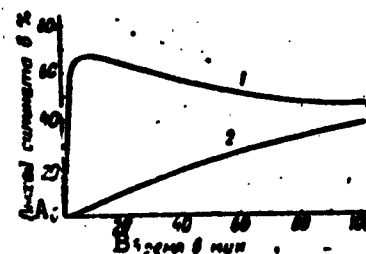A) Time in hours.

Fig. 48. Curves of reaction
of MgO with SiO_2 (1:1) at
temperature of $1170°$. 1)
Mg_2SiO_4; 2) $MgSiO_3$. A) Yield
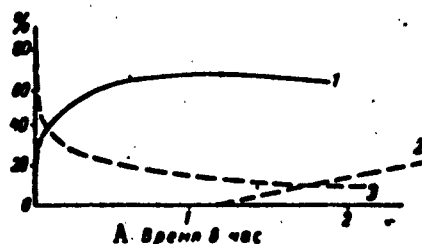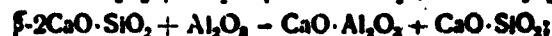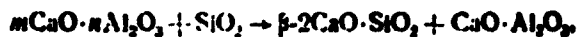of silicate in %; B) time in
minutes.

Fig. 49. Curves of reaction
of BaO with SiO_2 (1:1) at
temperature of $1010°$. 1)
Ba_2SiO_4; 2) $BaSiO_3$; 3) BaO.
A) Time in hours.

$$mCaO + nAl_2O_3 \rightarrow mCaO \cdot nAl_2O_3 \ (12:7),$$
$$2CaO + SiO_2 \rightarrow \beta\text{-}2CaO \cdot SiO_2 \ .$$

or

$$mCaO \cdot nAl_2O_3 + SiO_2 \rightarrow \beta\text{-}2CaO \cdot SiO_2 + CaO \cdot Al_2O_3,$$
$$\beta\text{-}2CaO \cdot SiO_2 + Al_2O_3 - CaO \cdot Al_2O_3 + CaO \cdot SiO_2;$$

then the calcium metaaluminate and metasilicate react with one another to form helenite:

$$CaO \cdot Al_2O_3 + CaO \cdot SiO_2 \rightarrow 2CaO \cdot Al_2O_3 \cdot SiO_2$$

and, finally, the reaction between the helenite and the remaining silicon dioxide yields anorthite

$$2CaO \cdot Al_2O_3 \cdot SiO_2 + 2SiO_2 \rightarrow CaO \cdot Al_2O_3 \cdot 2SiO_2 + CaO \cdot SiO_2.$$

Thus, helenite is one of the intermediate products in the process by which anorthite is formed from the oxides.

A scheme of the processes involved in producing helenite and anorthite from the oxides that differs somewhat from that described above but is also multistaged was described at one time on the basis of the experimental research of Yander and Petri [295].

According to the observations of Berezhnoy [292], the process by which three-component compounds are produced in the $CaO\text{-}MgO\text{-}SiO_2$ system — monticellite $CaO \cdot MgO \cdot SiO_2$ and mervinite $3CaO \cdot MgO \cdot 2SiO_2$ — also consists of a number of stages, the first of which is formation of $2CaO \cdot SiO_2$.

The stages in the synthesis reactions for braunmillerite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, celsian $BaO \cdot Al_2O_3 \cdot 2SiO_2$ and many other practically important minerals from crystalline oxides have recently been studied, as well as the extent of chemical conversion in complex charges encountered in the production of glasses, certain ceramics, and other materials [296, 297].

[Footnotes]

161   The majority of the elementary processes are individually
considered in Chapter 2.

169   See also the work described in [120] and [230].

193   A, B, C, etc. must be understood to represent: a) initial
reagents which are not decomposed during the course of the
process and b) substances to which the initial compounds
decompose under the conditions of the process.

199   Certain considerations and conclusions cited in Reference
[286] correspond almost word for word with those published
during the same period in References [57, 120, 234, et al.].

201   *In the presence of oxygen in less-than-excess quantity.

201   **At this temperature a portion of the sulfur can also react
with the silver, being in the vapor state.

209   The specific mechanisms underlying definite chemical proces-
ses in various crystalline mixtures are explained in de-
tail in Chapter 9.

[List of Transliterated Symbols]

193   т = t = tverdoye telo = solid

193   ж = zh = zhidkost' = liquid

193   г = g = gaz = gas = (also газ)

Chapter 4

THERMODYNAMIC CHARACTERIZATION OF REACTIONS

Thermodynamics enables us to establish the extent of a system's stability and the fundamental possibility of accomplishing a given process in it, as well as to formulate the thermodynamic probability of various reactions taking place in the system.

These important singularities of the thermodynamic method for investigating the processes has not as yet been adequately exploited by solid-state chemistry. Since the first reports of Tammann [211] on the thermodynamics of reactions in crystalline mixtures were published, relatively few papers have appeared in this field (only beginning with the nineteen-fifties do we observe a certain shift in this direction). This is to be accounted for in part by the limited volume of exact data available on the thermal properties of the solids at the high temperatures characteristic for many reactions in solid mixtures.*

As we have already noted, a process goes spontaneously in the direction that reduces the thermodynamic potential Z of the system to a certain value that is minimal for the prevailing conditions. Of the series of processes that may take place in the system, the thermodynamically most probable is that one which is accompanied by the largest drop in Z. The thermodynamic-potential reduction ΔZ expresses the maximum work of the process at a constant pressure $A_p = -\Delta Z$ and characterizes the so-called "chemical affinity" between the substances, i.e., their tendency to react chemically with one another.

Since Z is the isobaric (strictly speaking, isobaric-isothermal)

thermodynamic potential of the system, i.e., characterizes its state
at p = const, it incorporates the work of expansion of the system

$$Z = U - TS + pV \qquad (84)$$

or

$$Z = H - TS. \qquad (84a)$$

where U and TS are, respectively, the internal and bound energies of
the system, if T is the absolute temperature and S is the entropy,
while H = (U + pV) is the enthalpy.

We may frequently judge the thermodynamic probability of a pro-
cess on the basis of the change in free energy F as determined from

$$F = U - TS. \qquad (85)$$

Actually, the maximum work of a reversible isothermal process at
constant volume is equal to the loss of free energy

$$A_V = -\Delta F.$$

We may also operate with this value in all cases in which the
volume change is for all practical purposes nonessential, when $\Delta F \cong$
$\cong \Delta Z$. We observe this situation during the course of many reactions in
crystalline mixtures. However, if the process is accompanied by a con-
siderable change in the volume of the solid, as is the case, for
example, in certain polymorphic transformations (§1 of Chapter 9),
characterizing it thermodynamically will require calculation of ΔZ.

In the case of polymorphic transformation, the thermodynamic sta-
bility condition of a given modification and a given temperature is
attainment of the minimum of Z (or F), as determined from Equations
(84a and 85). Here, the entropy S may be regarded as a quantity char-
acterizing the extent to which the crystalline structure of the solid
deviates from ideal order. Since the role of the entropy term in
Equation (85) acquires greater significance with increasing tempera-
ture, the modification with the greater internal energy may possess a

smaller free energy, i.e., it may become more stable; as a result, the body goes into the new modification.*

As for chemical reactions in the crystalline phases, even van't Hoff [298] succeeded in showing that strictly solid-phase reactions reach equilibrium only when mixed crystals are formed. Subsequently, Tammann [211] applied this rule to various types of reactions taking place during heating of mixtures of crystalline solids.

According to Tammann, such reactions go in the direction of heat evolution until one of the reagents is exhausted; equilibrium can intervene only under certain, rather improbable conditions (page 166).

Actually, it is clear from the equation of variation of the isobaric thermodynamic potential

$$\Delta Z = \Delta H - T\Delta S \tag{86}$$

that ΔZ may approach zero only in the following cases:

1) when the heat of formation of the reaction product is extremely small: here, ΔH is a small quantity, and the difference $(\Delta H - T\Delta S) \to 0$;

2) when mutual solubility of the phases, formation of mixed crystals, glasses, etc., are possible; all of these processes result in an increase in ΔS;

3) when there is a considerable difference between the sum of the heat capacities of the initial reagents and the reaction products: this may have a noticeable influence on the entropy since $S_{\tau} = \int_{\circ}^{\tau} \frac{c_p}{T} dT$;

4) when gases or liquids take part in the reaction: here, ΔS may reach rather large values and it is possible, particularly at high temperatures, for $T\Delta S \to \Delta H$, i.e., $(\Delta H - T\Delta S) \to 0$.

It is normally assumed that the liberation of a heat $q > 1$ kcal/ g-atom is sufficient for a reaction to take place between solid phases. In actuality, the heat of formation of the products of many reactions

in crystalline mixtures reach much higher values. For example, the heat is reckoned in tens and hundreds of kilocalories per mole for the majority of silicate systems. From the thermodynamic standpoint, therefore, these reactions can and should go to completion with evolution of heat, provided that gaseous and liquid substances do not participate in them (in practice, the possibility of completion of the process may be severely limited by kinetic factors).

In cases where a process taking place on heating of a crystalline mixture is accompanied by the appearance of liquid or gaseous bodies or by the emergence of crystal-structure defects, i.e., by phenomena that increase the disorder in the system, it is distinguished by essential peculiar features.

On transition of a system into a more disordered state, its entropy naturally increases. For this reason, the term of Equation (84a) containing the entropy always operates in such a way that an increase in temperature "encourages" the reaction direction associated with an increase in the quantity of liquid or gaseous phase.

For example, this accounts for the fact that combustion of carbon at high temperatures takes place preferentially in accordance with the equation
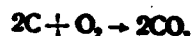
$$2C + O_2 \rightarrow 2CO,$$

although under any temperature conditions the reaction

$$C + O_2 \rightarrow CO_2$$
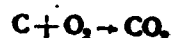
is accompanied by a considerably greater heat effect than the first. For the same reason, the reaction $C + CO_2 \rightleftharpoons 2CO$ goes spontaneously to the right at temperatures above 700-750°, despite the fact that this involves a considerable endothermic effect.

The increase in entropy with increasing number of gaseous molecules in the system is generally so essential that the value of the

product TΔS exceeds the heat effect of the reaction. It is precisely
for this reason that the van't Hoff rule, which states that only exo-
thermic reactions take place in solids, loses its validity when gaseous
and liquid substances participate in the reaction.

In cases where gaseous substances participate at high tempera-
tures, the process most often goes in the reverse direction. When
dissolved substances participate in the process, it is generally diffi-
cult to speak of any relationship whatsoever between the direction of
the reaction and the sign of its heat effect, since the change in en-
tropy on solution of the substance may be either positive or negative.

Rigorous solution of the basic problems in thermodynamic investi-
gation of high-temperature processes in solid mixtures requires, as
noted by Mchedlov-Petrosyan [299, 300], among others, careful account-
ing for: a) the influence of pressure on the processes that are ac-
companied by an essential change in phase volume (if the process is
being run under a pressure that differs considerably from atmospheric),
b) phase transformations of the components in the temperature range of
the process and c) the change in entropy and heat capacity with
temperature.

The new methods of computing entropy that have been developed by
Kireyev [301], Kapustinskiy and Yatsimirskiy [302] and other investi-
gators, the entropy method of calculating the heat capacities of in-
organic solids at high temperatures that was proposed by Landia [303],
and the isoatome method of Shchukarev [304] for determining the enthal-
py of formation of compounds have opened wide possibilities for thermo-
dynamic analysis of reactions in mixtures of crystalline substances.

Also worthy of attention is the so-called "exact practical"
method of computing the equilibrium constants that was proposed by
Vladimirov [329].

Here we can only give a brief description of the methods cited above.

In view of the imperfection and limited applicability of methods for computing heat capacity that are based on a model of an elastic continuum consisting of harmonic oscillators, Landia proposed [303] that the heat capacities of inorganic solid compounds be computed from their entropies.

According to quantum theory, entropy and heat capacity are functions of a single argument θ/T, where θ is the so-called "characteristic temperature," which is proportional to the natural-vibration frequency (which depends on the kind of solid), and T is the absolute temperature.

TABLE 19

Calculated and Experimental Values of Heat Capacities for Certain Compounds

1 Соединение	2 Температура в град. K	3 Теплоемкость C_p в кал/моль·град.		
		4 экспериментальная	5 рассчитанная по Ландау	6 $C_p = \Sigma C_p$ окислов
Fe₂SiO₄	1373	49.4	47.5	46.7
FeTiO₃	1573	34.5	34.3	33.7
MgSiO₃	1573	31.7	32.4	30.5
MgTiO₃	1773	33.9	34.0	31.9
CaSiO₃	1373	31.4	31.8	33.0
Ca₂SiO₄	1573	49.7	51.4	53.0
Ca₃SiO₅	1773	63.6	62.5	73.96
SrTiO₃	1400	30.5	32.9	35.2
Sr₂TiO₄	1600	44.4	46.9	52.0
BaTiO₃	1600	32.1	33.9	38.2
Ba₂TiO₄	1400	44.9	45.8	50.6

1) Compound; 2) temperature in degrees K; 3) heat capacity C_p in cal/mole-degree; 4) experimental; 5) calculated after Landau; 6) of oxides.

Earlier, the Lindemann formula, which is applicable only for simple polar compounds, was most frequently used in calculating values of θ. In a departure from this, Landia proposed that the averaged frequency be computed from the known value of the compound's entropy
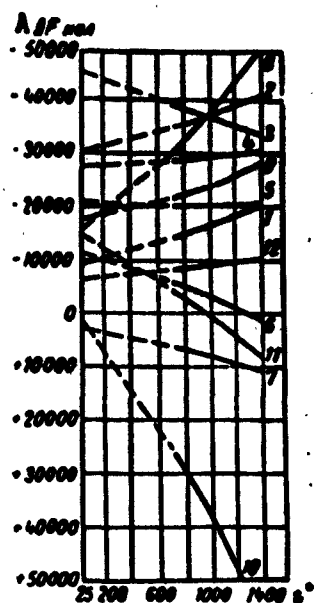
Fig. 50. Change in
free energy on for-
mation of calcium
silicates. A) ΔF,
cal.

or the value computed using sufficiently
exact methods [301, 302].

The advantages of this calculation method
proceed from the facts that a) the entropy
value can be found easily by the methods noted
and b) the entropy, which is a function of
the same argument as heat capacity, is more
representative of the factors influencing heat
capacity than are other constants of the com-
pound.

The Landia method gives heat-capacity
values that are closer to the experimental than
those obtained by other calculations. The data
on the heat capacities of certain silicates
and titanates that are listed in Table 19 [305]
provide a clear illustration of this.

The Shchukarev isoatome method [304] is based on consideration,
in general form, of the relationship between the composition of the
compounds in a system of two components and the values of their en-
thalpies of formation.

It is shown that if we refer the formation-enthalpy value of the
compounds to a single averaged gram-atom (i.e., divide the ΔH_{obr} per
gram-formula by the number of atoms $\underline{n}$ in the formula), this quantity
varies smoothly as we pass from one compound to another within the
limits of a certain pleiad of binary compounds. Consequently, in con-
structing a diagram of formation-enthalpy variation in the system of
compounds in the coordinates $\Delta H_{obr}/n$ versus molar composition, we ob-
tain a smooth curve — the isoatome. According to Shchukarev, the mono-
tonic nature of the isoatome is accounted for by the smooth variation

- 221 -

of the fraction of bonds between atoms of different elements and the fraction of bonds between atoms of a given element. An important property of the isoatome is that, as a rule, it possesses an extremum.

The nature of the isoatomes permits their use to find the formation enthalpies of the compounds by interpolation, and sometimes even by extrapolation.

Using the Landia method, Mchedlov-Petrosyan made a series of calculations at one time for the $MgO-SiO_2$ [306], $CaO-SiO_2$ [307], $Al_2O_3-SiO_2$, $CaO-Al_2O_3$ [308] systems and others.

The calculations pertaining to the $MgO-SiO_2$ system, which provide a basis for the known fact of primary formation therein of magnesium orthosilicate [293, 294, 309], the appearance of the metasilicate in the presence of MgO at temperatures above 1160° [310, 311] and certain other phenomena, would appear to require certain modifications: this is indicated by the direction taken by the individual curves on the diagram in Reference [306]. Later, using more reliable calculations (Table 20, Fig. 50), a thermodynamic basis was indicated for primary formation of the orthosilicate in the $CaO-SiO_2$ system [307], the impossibility of formation of $3CaO \cdot SiO_2$ due to solid-phase reactions was established, the improbability of the appearance of sillimanite rather than mullite in the reaction of Al_2O_3 with SiO_2 [308] and the highest probability of formation of mullite from dehydrated kaolinite were indicated, and so forth.

Table 20 presents data on the change in free energy in the $CaO-SiO_2$ system in the course of the following reactions:
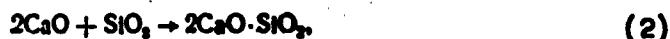
$$CaO + SiO_2 \rightarrow CaO \cdot SiO_2. \qquad (1)$$

$$2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2, \qquad (2)$$

$$3CaO + 2SiO_2 \rightarrow 3CaO \cdot 2SiO_2, \qquad (3)$$

$$3CaO + SiO_2 \rightarrow 3CaO \cdot SiO_2, \qquad (4)$$

$$CaO \cdot SiO_2 + CaO \rightarrow 2CaO \cdot SiO_2, \qquad (5)$$

$$2CaO \cdot SiO_2 + SiO_2 \rightarrow 2(CaO \cdot SiO_2), \qquad (6)$$

$$2CaO \cdot SiO_2 + CaO \rightarrow 3CaO \cdot SiO_2, \qquad (7)$$

$$3CaO \cdot 2SiO_2 + CaO \rightarrow 2(2CaO \cdot SiO_2), \qquad (8)$$

$$3CaO \cdot 2SiO_2 + SiO_2 \rightarrow 3(CaO \cdot SiO_2), \qquad (9)$$

$$3(2CaO \cdot SiO_2) + SiO_2 \rightarrow 2(3CaO \cdot 2SiO_2), \qquad (10)$$

$$2CaO \cdot SiO_2 + CaO + SiO_2 \rightarrow 3CaO \cdot 2SiO_2, \qquad (11)$$

$$CaO \cdot SiO_2 + 2CaO \rightarrow 3CaO \cdot SiO_2 \qquad (12)$$

TABLE 20

Change in Free Energy of $CaO-SiO_2$ System
During Various Reactions Taking Place in It
[307]

Номера реакций	Значение ΔZ в кал/моле при температурах (в град. K)					
	1000	1100	1200	1400	1600	1700
1	−20300	−20270	−20580	−20100	−20860	−20650
2	−35550	−36550	−36840	−38800	−40780	−41940
3	−39090	−38090	−37950	−36050	−34240	−33200
4	−28460	−28670	−29440	−29000	−30610	−31350
5	−14340	−15330	−16290	−18440	−19910	−21050
6	−6050	−4970	—	−2010	+350	+1520
7	+6160	—	+7440	+8860	+10110	+10720
8	−30460	—	−35970	−41780	−47840	−50790
9	−21770	−22360	−23530	−25270	−27910	−28840
10	+25990	+30510	+34590	+44340	+54000	+59090
11	−4360	−2820	−1650	+2800	+6670	−8060
12	−8080	—	−8750	−9520	−9990	−10390

1) Reaction No.; 2) value of ΔZ in cal/mole at
temperature of (degrees K).

A detailed thermodynamic analysis of reactions in the $CaSO_4-SiO_2$
system was made by Tshebatovskiy et al. [312]. The authors computed
the change in thermodynamic potential in the temperature range from
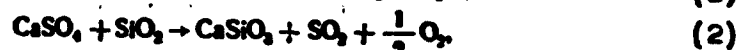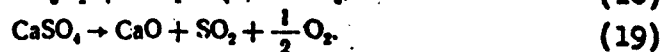1100 to $1700^\circ K$ for nineteen reactions that may occur in this system:

$$2CaSO_4 + SiO_2 \rightarrow Ca_2SiO_4 + 2SO_2 + O_2, \qquad (1)$$

$$CaSO_4 + SiO_2 \rightarrow CaSiO_3 + SO_2 + \frac{1}{2}O_2, \qquad (2)$$

$$3CaSO_4 + 2SiO_2 \rightarrow Ca_3Si_2O_7 + 3SO_2 + 1\frac{1}{2}O_2, \qquad (3)$$

$$3CaSO_4 + SiO_2 \rightarrow Ca_3SiO_5 + 3SO_2 + 1\frac{1}{2}O_2, \qquad (4)$$

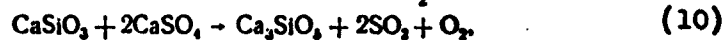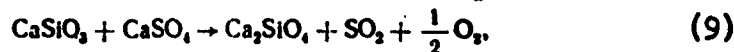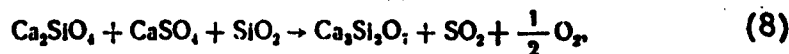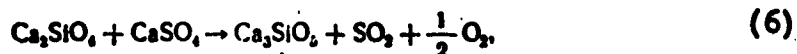$$Ca_2SiO_4 + SiO_2 \rightarrow 2CaSiO_3, \qquad (5)$$
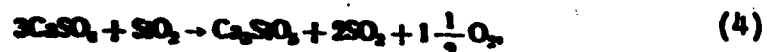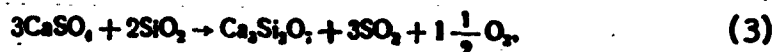
TABLE 21

Change in Thermodynamic Potential of $CaSO_4$-SiO_2 System During Course of Various Reactions in It [312]

Номера реакций	Значение ΔZ в кал при температурах в град. К						
	1100	1200	1300	1400	1500	1600	1700
1	+53 670	+40 515	+27 541	+14 735	+2 402	−9 256	−20 636
2	+25 461	+19 402	+13 434	+7 580	+1 876	−3 490	−8 690
3	+83 320	+64 750	+46 491	+28 543	+11 250	−4 770	−20 797
4	+102 281	+83 495	+65 015	+46 837	+29 340	+12 900	−3 169
5	−2 495	−1 499	−438	+377	−1 294	+2 240	+3 205
6	+48 630	+43 005	+37 500	+32 120	+26 566	+22 190	+17 569
7	+5 690	+8 050	+10 430	+12 923	+15 376	+17 912	+20 410
8	+29 652	+24 240	+18 757	+13 800	+8 855	+4 269	−156
9	+28 190	+21 115	+14 108	+7 164	+532	−5 770	−11 950
10	+76 811	+64 106	+51 595	+39 294	+27 510	+16·33	+5 626
11	+23 977	+16 222	+8 528	+883	−6 520	−13 618	−20 581
12	−6 903	−6 571	−6 220	−5 848	−5 696	−5 544	−5 339
13	−18 930	−18 711	−18 484	−18 252	−18 043	−17 826	−17 635
14	+5 026	−2 500	−9 970	−17 382	−24 577	−31 460	−38 210
15	−43 607	−45 510	−47 47?	−49 500	−51 547	−53 652	−55 770
16	−25 858	−25 312	−24 738	−24 150	−23 797	−23 427	−23 036
17	+32 394	+25 984	+19 666	+13 427	+7 564	−2 054	−3 355
18	−4 210	−4 892	−5 583	−6 255	−7 038	−7 820	−8 500
19	+43 050	+36 890	+30 843	+24 909	+19 210	+13 876	+8 600

1) Reaction No.; 2) value of ΔZ in cal at temperature of (degrees K).

$$Ca_2SiO_4 + CaSO_4 \rightarrow Ca_3SiO_5 + SO_2 + \tfrac{1}{2}O_2, \tag{6}$$

$$3Ca_2SiO_4 + SiO_2 \rightarrow 2Ca_3Si_2O_7, \tag{7}$$

$$Ca_2SiO_4 + CaSO_4 + SiO_2 \rightarrow Ca_3Si_3O_7 + SO_2 + \tfrac{1}{2}O_2, \tag{8}$$

$$CaSiO_3 + CaSO_4 \rightarrow Ca_2SiO_4 + SO_2 + \tfrac{1}{2}O_2, \tag{9}$$

$$CaSiO_3 + 2CaSO_4 \rightarrow Ca_3SiO_5 + 2SO_2 + O_2, \tag{10}$$

$$Ca_3Si_2O_7 + CaSO_4 \rightarrow 2CaSi_2O_4 + SO_2 + \tfrac{1}{2}O_2, \tag{11}$$

$$\left. \begin{array}{l} Ca_3Si_2O_7 + SiO_2 \rightarrow 3CaSiO_3, \\ Ca_3SiO_5 + SiO_2 \rightarrow Ca_3Si_2O_7, \end{array} \right\} \tag{12} \\ \tag{13}$$

$$Ca_3SiO_5 + SiO_2 + CaSO_4 \rightarrow 2Ca_2SiO_4 + SO_2 + \tfrac{1}{2}O_2, \tag{14}$$

$$\left. \begin{array}{l} 2Ca_3SiO_5 + SiO_2 \rightarrow 3Ca_2SiO_4, \\ Ca_2SiO_4 + 2SiO_2 \rightarrow 3CaSiO_3, \end{array} \right\} \tag{15} \\ \tag{16}$$

$$2CaSiO_3 + CaSO_4 \rightarrow Ca_3Si_2O_7 + SO_2 + \tfrac{1}{2}O_2, \tag{17}$$

$$Ca_3Si_2O_7 \rightarrow Ca_2SiO_4 + CaSiO_3, \tag{18}$$

$$CaSO_4 \rightarrow CaO + SO_2 + \tfrac{1}{2}O_2. \tag{19}$$

The results of the calculations, which are presented in Table 21 and Fig. 51, enable us to tabulate the probabilities of the different reactions in the region of relatively low temperatures

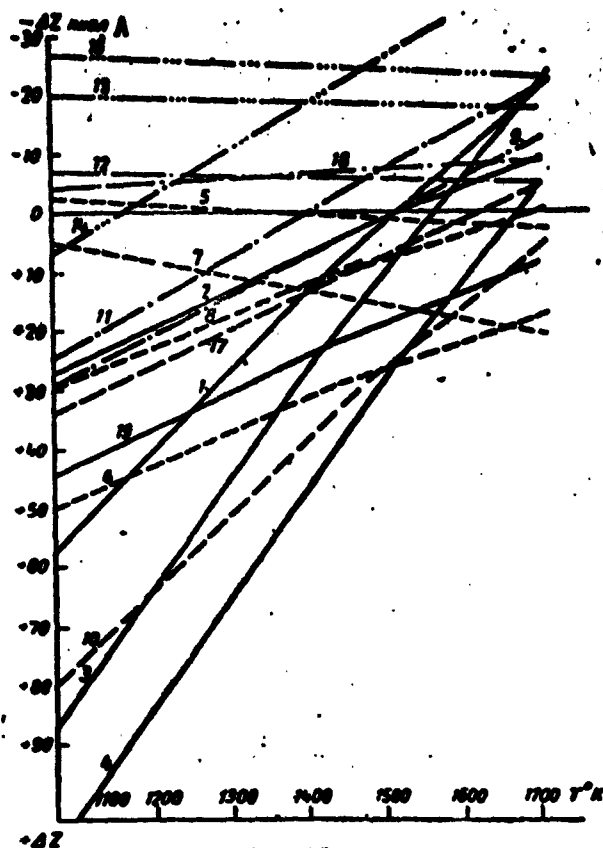(1100-1500°K or ~800 to 1200°) and relatively high temperatures (1500-1700°K or ~1200-1400°).

Fig. 51. Variation of thermodynamic potential during reactions in the $CaSO_4 + SiO_2$ system. A) $-\Delta Z$, kcal.

It is clear that among the primary processes (1-4) in which silicates appear in the region of relatively low temperatures, the most probable from the thermodynamic standpoint is formation of $CaSiO_3$ by reaction (2), which involves the lowest value of ΔZ, followed by the formation of Ca_2SiO_4 by reaction (1), which is characterized by a larger temperature coefficient of ΔZ. Unlike Ca_2SiO_4, which reacts with quartz by reaction (5) and $Ca_3Si_2O_7$, which can decompose into Ca_2SiO_4 and $CaSiO_3$ by reaction (18) and react with SiO_2 to form $CaSiO_3$ by reaction (18) and react with SiO_2 to form $CaSiO_3$ by reac-

- 225 -

tion (12), the silicate of composition $CaSiO_3$ is thermodynamically stable over this entire temperature range.*

In the region of higher temperatures, reaction (1), in which Ca_2SiO_4 forms, becomes most probable from an energy standpoint. The probability that it will vanish in accordance with (5) in this region is greatly reduced. $CaSiO_3$ is unstable: reaction (9) converts it to Ca_2SiO_4. The probability of formation of $Ca_3Si_2O_7$ by (3) becomes considerable only at a temperature of about $1400°$, since if it appears at lower temperatures it is converted into Ca_2SiO_4 in accordance with (11). Moreover, the $Ca_3Si_2O_7$ that has appeared decomposes, as noted above, into the ortho- and metasilicates in accordance with (18).

Certain of these conclusions enable us to refine and supplement our thermodynamic characterization of the processes in which calcium silicates form, as it was given earlier by other investigators.

The thermodynamic conditions of formation of barium silicate [305, 313] and strontium silicate [305] have been studied on a number of occasions. The most detailed and rigorous thermodynamic investigation of the $BaO-SiO_2$ and $SrO-SiO_2$ systems was made by Glushkova [305]. The author compiled the enthalpies of formation of the silicates of barium and strontium — partly from literature data and partly from estimates using the isoatome method — and the heat capacities of certain compounds belonging to these systems, as computed by the Landia method, and used these data as a basis for deriving equations for the temperature dependence of the free-energy change for the following twenty-nine reactions:

$$BaO + SiO_2 \rightarrow BaSiO_3. \tag{1}$$
$$2BaO + SiO_2 \rightarrow Ba_2SiO_4. \tag{2}$$
$$3BaO + SiO_2 \rightarrow Ba_3SiO_5. \tag{3}$$
$$BaO + 2SiO_2 \rightarrow BaSi_2O_5. \tag{4}$$

$$BaO_2 \rightarrow BaO + \frac{1}{2} O_2, \qquad (5)$$

$$BaO_2 + SiO_2 \rightarrow BaSiO_3 + \frac{1}{2} O_2, \qquad (6)$$

$$2BaO_2 + SiO_2 \rightarrow Ba_2SiO_4 + O_2, \qquad (7)$$

$$3BaO_2 + SiO_2 \rightarrow Ba_3SiO_5 + \frac{3}{2} O_2, \qquad (8)$$

$$BaO_2 + 2SiO_2 \rightarrow BaSi_2O_5 + \frac{1}{2} O_2, \qquad (9)$$

$$BaO_2 + BaSiO_3 \rightarrow Ba_2SiO_4 + \frac{1}{2} O_2, \qquad (10)$$

$$BaCO_3 \rightarrow BaO + CO_2, \qquad (11)$$

$$BaCO_3 + SiO_2 \rightarrow BaSiO_3 + CO_2, \qquad (12)$$

$$2BaCO_3 + SiO_2 \rightarrow Ba_2SiO_4 + 2CO_2, \qquad (13)$$

$$3BaCO_3 + SiO_2 \rightarrow Ba_3SiO_5 + 3CO_2, \qquad (14)$$

$$BaCO_3 + Ba_2SiO_4 \rightarrow Ba_3SiO_5 + CO_2, \qquad (15)$$

$$2BaCO_3 + BaSiO_3 \rightarrow Ba_3SiO_5 + 2CO_2, \qquad (16)$$

$$BaCO_3 + BaSiO_3 \rightarrow Ba_2SiO_4 + CO_2, \qquad (17)$$

$$BaCO_3 + 2SiO_2 \rightarrow BaSi_2O_5 + CO_2, \qquad (18)$$

$$4BaCO_3 + SiO_2 \rightarrow Ba_4SiO_6 + 4CO_2, \qquad (19)$$

$$2Ba_3SiO_5 + SiO_2 \rightarrow 3Ba_2SiO_4, \qquad (20)$$

$$SrCO_3 \rightarrow SrO + CO_2, \qquad (21)$$

$$SrCO_3 + SiO_2 \rightarrow SrSiO_3 + CO_2, \qquad (22)$$

$$2SrCO_3 + SiO_2 \rightarrow Sr_2SiO_4 + 2CO_2, \qquad (23)$$

$$3SrCO_3 + SiO_2 \rightarrow Sr_3SiO_5 + 3CO_2, \qquad (24)$$

$$SrCO_3 + SrSiO_3 \rightarrow Sr_2SiO_4 + CO_2, \qquad (25)$$

$$SrO_2 \rightarrow SrO + \frac{1}{2} O_2, \qquad (26)$$

$$SrO + SiO_2 \rightarrow SrSiO_3 \qquad (27)$$

$$2SrO + SiO_2 \rightarrow Sr_2SiO_4, \qquad (28)$$

$$3SrO + SiO_2 \rightarrow Sr_3SiO_5. \qquad (29)$$

The values of the free-energy changes according to reactions (1-29) are presented in Figs. 52 and 53 as computed in Reference [305]. Examination of these diagrams enables us to compile the thermodynamic probabilities of the various reactions and, accordingly, the probabilities of formation of the various compounds in the systems studied.

Among other things, it follows from Fig. 52 that at temperatures below 700-750°, only barium metasilicates can form in mixtures of silicon dioxide with barium carbonate in a carbon-dioxide medium or,
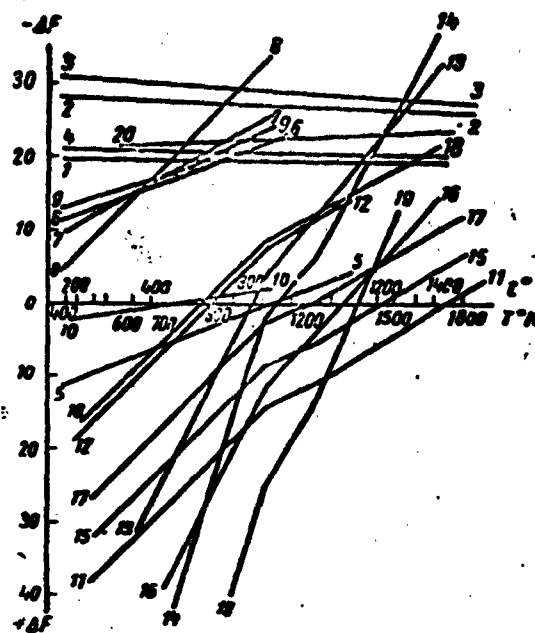
Fig. 52. Change in free energy on
formation of barium silicates.
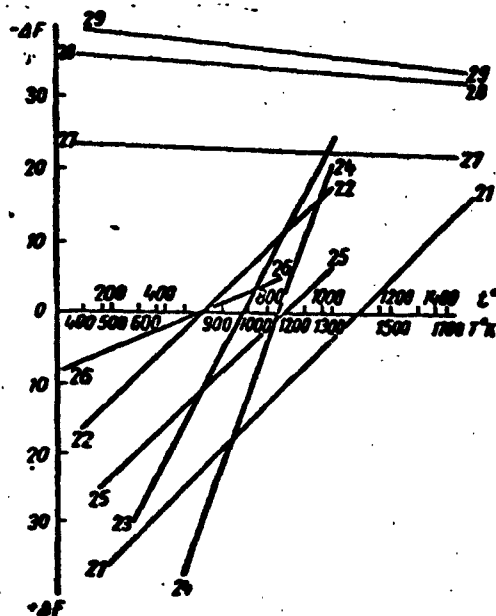
Fig. 53. Change in free energy on
formation of strontium silicates.

in the case of a large excess of silicon dioxide, $BaSi_2O_5$. At tempera-
tures above $750°$, barium orthosilicate may form simultaneously with

the metasilicate (curve 13), while at temperatures above 800°, formation of Ba_2SiO_4 is thermodynamically more probable than that of $BaSiO_3$.

At these temperatures, the metasilicate present in the system may interact with the unreacted $BaCO_3$ and be converted to the orthosilicate. Consequently, as long as there is barium carbonate on the interface, barium orthosilicate forms preferentially. At temperatures above 900° in mixtures rich in barium carbonate, there is a possibility of formation of tribarium silicate, either from the initial components or by reaction of $BaCO_3$ with the barium meta- and orthosilicates (see Fig. 52, curves 14-16).

In SiO_2-rich mixtures, reactions with the excess of silicon dioxide should take place after complete bonding of the barium into the ortho- and tribarium silicates and result in the formation of the metasilicate.

A similar pattern should be observed in synthesis of barium silicates from barium peroxide and silicon dioxide: at relatively low temperatures, $BaSiO_3$ and $Ba_2Si_3O_8$ form preferentially, while at high temperatures we see preferential formation of barium orthosilicate and tribarium silicate (see Fig. 52, curves 6-10).

Examination of the characteristics of the free-energy change that takes place in formation of the various strontium silicates (Fig. 53) enables us to evaluate the probability of their formation at various temperatures in just as detailed a manner.

It should be noted that the results of the experimental investigations of Keler and Glushkova [314] fully confirm reasoning concerning the reactions in the systems examined above that proceeds from thermodynamic calculations based on estimates of the compound-formation enthalpies by the isoatome method.

On the basis of the calculations that he undertook, Matveyev [315]

gave a thermodynamic characterization of the reactions in the CaO-Al_2O_3 system. Here he considered four primary reactions in which the basic compounds possible in the system are formed from the oxides:

$$3CaO + Al_2O_3 \rightarrow 3CaO \cdot Al_2O_3,$$
$$12CaO + 7Al_2O_3 \rightarrow 12CaO \cdot 7Al_2O_3,$$
$$CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3,$$
$$CaO + 2Al_2O_3 \rightarrow CaO \cdot 2Al_2O_3$$
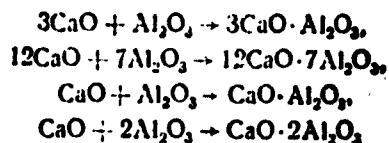
and "derivative" reactions of the type

$$(mq - np)CaO + n(pCaO \cdot qAl_2O_3) \rightarrow q(mCaO \cdot nAl_2O_3)$$

and

$$(np - mq)Al_2O_3 + m(pCaO \cdot qAl_2O_3) \rightarrow p(mCaO \cdot nAl_2O_3).$$
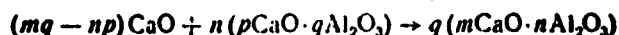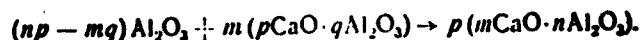
On compiling the ΔZ-values that he had calculated, Matveyev arrived at the following conclusions: From the thermodynamic standpoint, formation of the compounds $3CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$ is most probable in the system (this is in agreement with data on the actual composition of Portland cement) [316]; this does not exclude the formation of the compounds $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$ from the oxides; in the presence of free calcium oxide, compounds with large aluminum-oxide contents will be converted into compounds with smaller contents; the reverse conversion is improbable from a thermodynamic standpoint; in a mixture of CaO with γ-Al_2O_3, this sequence of compound formation is quite probable:

$$CaO \cdot 2Al_2O_3 \rightarrow CaO \cdot Al_2O_3 \rightarrow 12CaO \cdot 7Al_2O_3 \rightarrow 3CaO \cdot Al_2O_3.$$
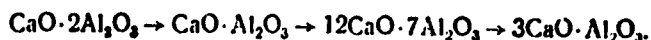
The author notes correctly that the stoichiometric proportions and the kinetic factors governed by the structural peculiarities of the reagents may play a certain part in the formation of the various compounds in this system.

In a paper published in 1958, Matveyev [315] expounds a method of approximate calculation of certain properties of compounds belonging to systems of the type MeO-RO_2 and MeO-R_2O_3; this method is based on application of structural principles to thermodynamic phenomena.

Thermodynamic investigation of high-temperature processes in oxide-carbon, sulfate-carbon and other similar systems is of great interest; this applies particularly to the $CaSO_4$ + C system, which is of great industrial importance [317-321].

The reaction in a mixture of calcium sulfate with carbon may consist of many reactions, which are accompanied by formation of various products [317-319]. There exist a wide variety of conceptions as to the essential nature and sequence of these reactions, and concerning their relative importance in the mechanism of the over-all decomposition process of the above mixture [317-319, 322, 323]. For this reason, the possibility of clearing up these problems by thermodynamic analysis is extremely attractive.

Such analysis was carried out in greatest detail by Volkov [324] in a study carried out under the supervision of one of the authors. Volkov computed the change in the isobaric-isothermal potential in the temperature range from 700 to 1100° for ten reactions of this system:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2, \tag{1}$$
$$CaSO_4 + 4C \rightarrow CaS + 4CO, \tag{2}$$
$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2, \tag{3}$$
$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2, \tag{4}$$
$$3CaS + CaSO_4 \rightarrow 4CaO + 2S_2, \tag{5}$$
$$2CaS + SO_2 \rightarrow 2CaO + 1{,}5S_2, \tag{6}$$
$$CaS + 2SO_2 \rightarrow CaSO_4 + S_2, \tag{7}$$
$$4CaO + 6SO_2 \rightarrow 4CaSO_4 + S_2, \tag{8}$$
$$2SO_2 + 4C \rightarrow 4CO + S_2, \tag{9}$$
$$2SO_2 + 4CO \rightarrow 4CO_2 + S_2. \tag{10}$$
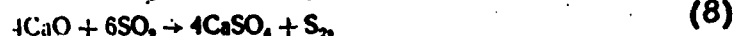
The calculations were carried out in accordance with the equation

$$\frac{\Delta Z_T}{T} = \frac{\Delta H_{298}}{T} - \Delta S_{298} - \Delta a_0 \int_{298}^{T} \frac{dT}{T^2} \int_{298}^{T} dT - \Delta a_1 \int_{298}^{T} \frac{dT}{T^2} \int_{298}^{T} T dT - $$
$$- \Delta a_2 \int_{298}^{T} \frac{dT}{T^2} \int_{298}^{T} T^2 dT - \Delta a_{-2} \int_{298}^{T} \frac{dT}{T^2} \int_{298}^{T} T^{-2} dT. \tag{87}$$

Change in Thermodynamic Potential During Various Reactions in $CaSO_4$ + C System

Номера реакций	2 Значения ΔZ в кал при температурах в град.							
	700	800	850	900	950	1000	1050	1100
1	-44 866	-53 069	-57 113	-61 133	-65 133	-69 094	- 73 033	- 76 938
2	-45 106	-61 696	-69 939	-78 144	-86 294	-94 117	- 102 492	-110 526
3	-44 619	-14 407	-45 275	-44 123	-43 960	-43 759	- 43 558	- 43 337
4	73 960	56 877	48 520	40 239	32 010	23 868	15 745	7 827
5	65 101	57 521	53 799	50 093	46 358	42 651	39 033	35 496
6	30 333	28 889	28 186	27 475	26 763	26 056	25 346	24 648
7	- 4 428	322	2 617	4 927	7 302	9 421	11 644	13 786
8	-78 388	-56 631	-45 915	-35 312	-24 812	-14 450	- 4 208	5 905
9	-49 573	-61 449	-67 390	-73 275	-79 175	-85 060	- 90 914	- 96 802
10	-49 016	-43 592	-41 152	-38 738	-36 416	-33 942	- 31 596	- 29 248

1) Reaction No.; 2) values of ΔZ in cal at temperatures (in degrees).

Here, the thermochemical data (values of ΔH_{298} and S_{298}) necessary for computing ΔZ_t were taken from References [325-327], the values of the integrals from the tables of Shvartsman and Temkin [328], and the values of the coefficients Δa_0, Δa_1 and so forth were found from sufficiently exact equations for the temperature dependence of the heat capacities of the corresponding solids [325-327].

Table 22 shows the results of these calculations.

The data of Table 22 and Fig. 54 enable us to draw certain conclusions concerning the course taken by individual reactions in the $CaSO_4$ + C system.

It is clear, for example, that in the temperature range studied, reactions (4-6) are thermodynamically improbable; nor can reaction (7) take place above 800°. Reduction of calcium sulfate by carbon at temperatures above 800° should take place preferentially by reaction (2), with formation of carbon monoxide; this is in agreement with the data of Gofman and Mostovich [247].

Of the reactions in which sulfur forms by reduction of SO_2 by carbon and its monoxide, reaction (9) is thermodynamically most probable. When these reducers are present in inadequate quantities
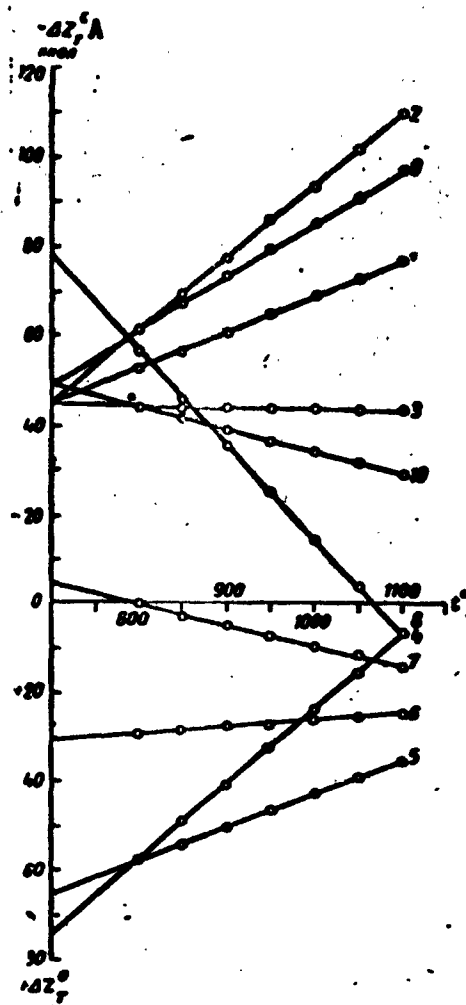
Fig. 54. Change in thermodynamic
potential during reactions in
$CaSO_4$ + C system. A) kcal.

for the reaction to take place at temperatures lower than 1070°, sulfur may also be formed by reaction (8).

The data obtained in the calculation not only account for certain experimentally established phenomena (e.g., the observed higher consumption of calcium sulfide than that necessary for reaction (4) [323]), but also facilitate selection of process conditions in conformity with the purpose of the process.

The influence of the conditions prevailing in the reactions on

- 233 -

their course has been established in a similar fashion for many other reactions in mixtures of crystalline solids.*

What is essential is that correct comparative characterization of the probabilities of the various reactions in a system on the basis of calculations similar to those described above is possible only for the ideal case of strictly solid-phase reactions. Participation of small quantities of gaseous or liquid phases in the chemical-conversion process of the reaction mixture may radically change the pattern of the process (see §4, Chapter 3).

It is no less important that thermodynamic considerations and calculations may, in general, be found inadequate as a basis for judgments to the effect that a reaction must necessarily proceed in a given direction if the conditions that determine its kinetics are not taken into consideration.

A high activation-energy value, large grain size and small contact area between the reagents and, finally, a high diffusion resistance to the process may make the unfolding of a thermodynamically probable reaction practically impossible. This applies particularly to reactions in crystalline mixtures.

For this reason, correct conclusions as to the course taken by such reactions are possible only as a result of complex thermodynamic and kinetic investigation of these reactions.

Manu-script Page No.	[Footnotes]
215	A large amount of information on the thermochemical data of the silicates will be found in the monograph of V. Eytel', Termokhimiya silikatov [Silicate Thermochemistry], Prom-stroyizdat, 1957.
217	This problem is illuminated in greater detail in §5 of Chapter 2.
226	The line expressing the change in Δz in accordance with reaction (15), which is not shown in Fig. 51, is situated much higher than line 16, as will be seen from the tabulated data.
234	The calculation is simplified considerably by the previously mentioned Vladimirov method [329], which is based on use of the additive property of the equilibrium constants of complex reactions and preliminary tabulation of a number of functions related to them. Use of the auxiliary table compiled by the author makes it possible to obtain easily the value of the equilibrium-constant logarithm for any complex heterogeneous reaction. Here, the accuracy of the calculation corresponds to the third Ulikh approximation and to the Temkin-Shvartsman method.

Manu-script Page No.	[List of Transliterated Symbols]
221	обр = obr = obrazovaniye = formation

Chapter 5

KINETICS

§1. HISTORY OF STUDY OF THE PROBLEM

The kinetics of reactions in crystalline mixtures is one of the most important and complex problems of their theory. At the same time, relatively few students have been concerned until recently with the relationships controlling the rates of these reactions.

The first attempts to establish relationships in this field were undertaken by Tammann.

Studying the reactions between thin plates of copper and tungsten oxides, Tammann [211] established that the rate of this process may be expressed by the equation

$$\frac{dx}{d\tau} = \frac{K}{\tau} \tag{88}$$

or

$$x = K \ln \tau + C, \tag{89}$$

where x is the thickness of the product layer, τ is the time, and K is a constant that depends on the properties of the reagents and the conditions of the process.

Some time later, proceeding from the fact that the limiting stage of the solid-phase process is diffusion of a reagent through the product layer and arbitrarily regarding the diffusion layers on the surfaces of the powdered-reagent granules as flat and using the familiar relationship of Fik for the diffusion rate through flat layers, Yander [221, 330] showed that under isothermal conditions, the rate of such

a process must be subject to the equation

$$\frac{dx}{dt} = \frac{K_1}{x}$$ (90)

or

$$x = K\sqrt{\tau}.$$ (91)

Here,

$$K = \frac{K'DC_0}{R_z^2}.$$ (92)

where K' is a constant that depends on the properties of the reagents and the process conditions, C_0 is the concentration of the diffusing reagent at the external surface of the diffusion layer of product, D is the diffusion coefficient of this reagent in this layer and R_z is the initial grain radius of the reagent that becomes coated by the product layer in the reaction process.
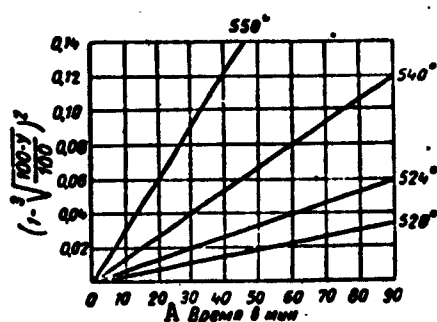
Fig. 55. Kinetics of reaction $CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2$ (after Yander). A) Time in minutes.

It should be noted that Equation (91) was derived earlier by Tammann [331, 332] for the rate of conversion of silver, copper and lead plates in an air medium containing halogens.

In view of the difficulty of experimental determination of the thickness $\underline{x}$ of the product layer in powder mixtures, Yander expressed it in terms of the degree of chemical conversion of the reagent coated by the product layer in the reaction process. This gave rise to the equation

$$\left(1 - \sqrt[3]{\frac{100-y}{y}}\right)^2 = K\tau,$$ (93)

where $\underline{y}$ expresses the extent of conversion of this reagent to the product in %.

Yander verified the validity of Equation (93) experimentally for

- 237 -
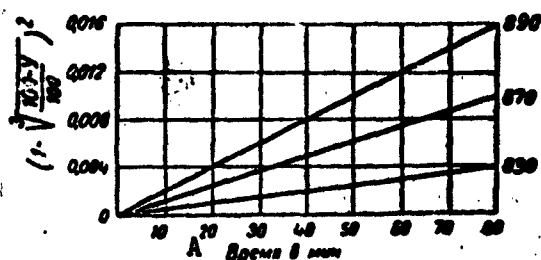
Fig. 56. Kinetics of reaction
$BaCO_3 + SiO_2 \rightarrow BaSiO_3 + CO_2$ (af-
ter Yander). A) Time in minutes.

the reactions of barium carbonate and calcium carbonate with silicon
monoxide, as well as that of calcium carbonate with molybdenum oxide.

In Yander's experiments, the acidic oxide was taken in a 10-fold
stoichiometric excess over the carbonate, and the values of the func-
tion $\left(1 - \sqrt[3]{\frac{100-y}{100}}\right)^2$ were computed from the degree of the latter's con-
version. Thus, the validity of Yander's Equation (93) was confirmed
experimentally, as shown by Figs. 55 and 56, which have been borrowed
from his work.

It should be noted that in the study under consideration, Yander
verified the validity of his equation preferentially for small degrees
of conversion of the reagents: in many of his experiments, the extent
of conversion of the carbonate was below 25%, in the overwhelming
majority of the experiments it was in the 40% range, and not once did
it exceed 80%. Furthermore, the method used by Yander to process the
experimental data cannot be theoretically justified. It is not admis-
sible to proceed in all calculations from the degree of conversion of
one of the reagents (for example, the carbonate, as was done in the
report being described) irrespective of which reagent produces the
more mobile particles. The fact of the matter is that Equation (93)
describes the change in the process rate as a function of the extent
to which the reagent that is "coated" by the diffusion layer and not

the diffusing reagent is converted. However, the difference between the conversion figures for the former and the latter may be (and, incidentally, was in Yander's experiments) exceedingly large.

It follows from Equation (92) that for a given value of R_z and a constant or linearly varying concentration C_0, the value of the coefficient K of Equation (93) should be proportional to the diffusion coefficient D.

Since the temperature dependence of the latter takes the form

$$D = Ae^{-\frac{E}{RT}},$$

then, according to Yander, the arbitrary rate constant of the reaction

$$K = C'e^{-\frac{E}{RT}},$$

where $C' = K'DC_0/R_3^2$, E is the so-called "softening" energy of the crystal lattice, R is the gas constant, and T is the absolute temperature.

Equation (93) presupposes an isothermal process.

To describe the kinetics of the exothermic reactions, which are accompanied by a change in temperature during the process, Yander [333] proposed the approximate equation

$$\left(1 - \sqrt[3]{\frac{100-y}{100}}\right)^2 = K\tau \exp\left[-CR\left(1 - \sqrt[3]{\frac{100-y}{100}}\right)\right]. \qquad (94)$$

where C depends on the heat effect of the reaction and $K = K_n/R^2$ if K_n is the coefficient in Equation (93) written for the initial time point of the reaction.*

The experimental verification of this equation undertaken by Yander on the reactions of barium carbonate with tungsten oxide and silver sulfate with lead oxide showed an insignificant disagreement between the data of calculations by Equation (94) and those from experiments. In a subsequent report [334], Yander noted that the rate of the reaction depends not only on the grain size of the reagents,

but also on the composition of the mixture, the method used in preparing it, the structure of the initial substances, and the structure of the reaction products, so that no definite numerical value of the coefficient K in Equation (93) can, in general, characterize a given reaction in different experiments.

Since Equation (93) had been verified only in mixtures characterized by a single constant proportion between the reagents, Yander noted in the same paper that, on the basis of study of the reactions of calcium carbonate with molybdenum oxide and barium carbonate with silicon oxide, the equation indicated remains valid for various relationships between the reagents in the initial mixture.

A significant number of papers by other authors who studied the kinetics of reactions in mixtures of solids are based on the idea that these reactions are all of the same type and, consequently, that their kinetic relationships can be described by a single equation. Here, the equations used most frequently were Yander's Equation (91) or Equation (93).

The authors of papers that followed this approach attempted to establish correspondence between the kinetics of the process that they were studying and Equation (91) or (93) or at least to find correction factors for them that would characterize the special nature of the process in question. Certain other investigators proceeded from the idea that it was possible to describe fully the kinetics of a given "solid-phase" chemical reaction over its entire course by an equation peculiar to this chemical reaction, in much the same way as is done for homogeneous systems. Here, efforts were made to ascertain a correspondence between the kinetics of the process being studied and equations of monomolecular, bimolecular or autocatalytic reaction in their usual form, or to obtain empirically a new equation that de-

scribed the kinetics of the reaction in question.

Examples of research in the first trend are the reports of Mamykin and Zlatkin [335], Zhuravlev et al. [336], Pol' and Teylor [337], and Gil'sen and Risel'berg [338], while research in the second trend is exemplified by the work of Khouers, Maskill and Terner [339] and the numerous studies of Yagich [223, 340 and others].

All of these investigations and many others, while they permitted us to establish certain important relationships pertaining to the problem under consideration, nevertheless left room for vagueness and contradiction on certain important points.

Thus, Equation (88) of Tammann was confirmed by the experiments of Tammann et al. [211, 331], Khedval and Yagich [340], Gil'sen and Risel'berg [338] and other authors.

On the other hand, on the basis of the experimental data that they obtained, many investigators indicated that Expression (88) was unsatisfactory for this purpose and that Equations (91) of Tammann and (93) of Yander were valid. In addition to Yander, Fishbek [341], Pol' and Teylor [337], Mamykin and Zlatkin [335], Bishof [342] and others arrived at the same conclusion as a result of their work.

Pol' and Teylor studied the reaction kinetics at 700-760° of soda mixed with quartz in 1:2 molar proportions and that of soda mixed with mullite with molar proportions of 1:3 and 1:1. The maximum degree of conversion reached 11% for the first reaction and 33% for the second reaction. In both cases, the authors observed an almost linear relationship between the values of the function $\left(1 - \sqrt{\frac{100-x}{100}}\right)^{2}$ of the extent of conversion of the soda and the time of the process at various temperatures. On this basis, they concluded the validity of Equation (93) for description of the kinetics of reactions of this type.

Mamykin and Zlatkin [335] investigated the kinetics of silicate formation in the system $CaO-SiO_2$ at temperatures of 800, 1200 and 1400°. On the basis of results obtained in roasting a mixture of these oxides at 1200° with a molar ratio $SiO_2/CaO = 25\%$, the authors computed values of the Yander function (Table 23) and concluded that the increase in the thickness of the reaction layer is proportional to the square root of time in accordance with Equation (93).

TABLE 23

Kinetics of Formation of Silicates in $CaO-SiO_2$ System (after Mamykin and Zlatkin)

1 Время в час.	2 Анализ в %		3 Процент реакции	$\left(1 - \sqrt{\frac{100-y}{100}}\right)^2$
	CaO	SiO₂		
0	3,5	96,5	0	0
0,25	1,5	95,2	56,28	$5,81 \cdot 10^{-2}$
0,5	1,1	—	65,7	$9,0 \cdot 10^{-2}$
1	1,0	—	70,0	$10,93 \cdot 10^{-2}$
3	0,8	94,6	76,57	$14,71 \cdot 10^{-2}$
6	0,4	94,5	88,0	$25,69 \cdot 10^{-2}$
9	0,3	94,5	91,4	$31,23 \cdot 10^{-2}$

1) Time in hours; 2) analysis in %; 3) "per cent reaction."

In connection with the last two papers, it is necessary to stress again that in studying the diffusion kinetics of a reaction in a solid mixture, we should employ in the calculations the values of the conversion ratio of the "coated" (and not of the diffusing) reagent. With a molar ratio of 2 between the silicon dioxide and the soda in the mixture, they react with one another, as shown by the data of Toropov [119], Lileyev [343] and one of the present authors [231], with formation of sodium metasilicate, i.e., in 1:1 proportions. For this reason, the degree of conversion of the SiO_2 in this mixture is always 1/2 that of Na_2CO_3. Since the diffusion layer of reaction product forms on the silicon dioxide granules in this case, values of the degree of conversion of this reagent should be substituted in the equa-

tion for the reaction kinetics.

When mullite reacts with soda, the "coated" reagent is the mullite, the extent of whose conversion into the product may not coincide with that of the soda with various proportions between the reagents in the initial mixture. The maximum "per cent reaction" (yield of product) according to estimates by Pol' and Teylor was always about 11, as indicated in their report, when the first process takes place (more properly, about 5.5), while for the second process it is about 33.

When calcium oxide reacts with silicon dioxide, the diffusing component is the first, and the "coated" component is the second of these reagents [118, 119, 277, 344]. Here, the layer of product formed on the silicon-dioxide grains offers resistance to diffusion, so that values of the extent of conversion of the SiO_2 must be substituted into Equation (93) in verifying the relationships of interest to us in the present case. Since, according to Mamykin and Zlatkin, the molar proportions between the SiO_2 and CaO were 25% and their reaction product was for the most part a silicate of the composition $3CaO \cdot 2SiO_2$ in the system that they studied, the degree of conversion of SiO_2 in the study indicated was 1/37.5 that of the CaO. For example, conversion of only 1.5% of the SiO_2 corresponded to 56% conversion of the CaO, while the highest degree of conversion of SiO_2 obtained in the experiments was below 2.5%.

According to this, all values of the Yander function that served as a basis for the derivations of Reference [335] will obviously change.

The above naturally restricts the possibility of using the results of References [221, 330-341] for generalizing conclusions as to the reaction kinetics in mixtures of solids.

In contradiction to the conclusions of Yander, Fishbek, Pol' and

Teylor, Mamykin and Zlatkin, the experimental investigations of Berezhnoy [1, 292], Zhuravlev et al. [336] and other authors indicate the highly relative accuracy of Equations (91) and (93) and the necessity of introducing correction factors into them in many cases that differ for different processes.

On the basis of a detailed investigation of reactions in mixtures containing chalcedony, Berezhnoy [292] concluded that Yander's Equation (93) is actually only approximate. Varying the grain size of magnesium and silicon oxides in an equimolar mixture of them, the author obtained various values for the extent of conversion of the MgO in different experiments lasting the same time (see Table 34). On this basis, he indicated that Yander's Equation (93) is applicable only for fine-grained mixtures with grains of approximately the same size.

Avgustinik and Kurdevanidze [345] studied the kinetics of the polymorphic transformation of silica and its reactions with calcium oxide (which was admittedly added in quantities of about 2% of the SiO_2 so that the degree of conversion of the latter into calcium silicate could have only negligible values) at temperatures between 1200 and 1500° and showed the inapplicability of Equation (93) for both of these processes.

Zhuravlev et al. [336] arrived in their time at the conclusion that Yander's Equation (93) was invalid for the process that they studied — that of formation of calcium aluminates at temperatures from 700 to 1380°. Apparently assuming that the concentration of the diffusing reagent on the outer surface of the diffusion layer of product varies in proportion to the extent of conversion of the second, "coated" reagent during the course of reactions in mixtures of solids, the authors of Reference [336] wrote as follows: "If we take into con-

sideration the influence of the changing concentration of the diffusing component, the basic differential equation of Yander assumes the following form:

$$\frac{dx}{dt} = \frac{KD}{x}(100 - y)^2.$$

From this, after expressing x in terms of R and y and integrating, it follows that

$$\left(\sqrt[3]{\frac{100}{100-y}} - 1\right)^2 = 200 K t. \tag{95}$$

This equation, which was derived on the basis of the assumption indicated, was found, according to the authors, to be more accurate in the case that they studied than Yander's Equation (93), but it nevertheless led to a considerable discrepancy between theory and experiment.

An attempt to use Equation (95) to describe the kinetics of the process in which magnesium silicates form, as reported later by Kutateladze and Lutsenko [311], was unsuccessful. The reason for this may consist in the lack of justification for assuming a direct dependence between the concentration of the diffusing component on the outside surface of the diffusion layer and the extent of conversion of the reagents. In a tremendous number of cases, this concentration may be regarded as constant, following Yander, over most of the process. In cases where it varies, it may be symbatic but not proportional to the extent of conversion of the "coated" reagent.

The reasoning of Pol' and Teylor [337] on the kinetics of reactions in solids are worthy of mention.

These authors assume that the kinetics of only "solid-phase" reactions can be described by Equation (91), while that of others (whose products do not accelerate or inhibit the reaction) can be described by the equation

$$\frac{dy}{dt} = K,\qquad\qquad(96)$$

while a third group (autocatalytic reactions) can be described by the equation

$$\frac{dy}{dt} = Ky.\qquad\qquad(97)$$

. Actually, as will be shown below, each of these equations is valid only in certain particular cases that lie within very narrow ranges of the process conditions, and these three equations are far from adequate for a generalized description of the kinetics of reactions in mixtures of solids.

Yagich also uses Formula (96) to describe the kinetics of a number of "solid-phase" reactions that he studied. In his work, which was done from 1942 to 1947 and in part referred to above, Yagich investigated the rate of reaction of silver sulfate and phosphate with magnesium oxide in a mixture of monodisperse powders of the reagents with the molar proportions between the MgO and the silver salt equal to 100. Then he studied the kinetics of the same reactions in polydisperse mixtures containing a stoichiometric excess of the silver salt.

Thereafter, Yagich investigated the rate of the reaction between tableted magnesium oxide and magnesium pyrophosphate:

$$MgO + Mg_2P_2O_7 \rightarrow Mg_3(PO_4)_2,$$
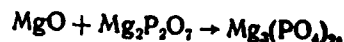
as well as that between lead oxide and lead silicates:

$$PbO + PbO \cdot SiO_2 \rightarrow 2PbO \cdot SiO_2,$$
$$2PbO + 2PbO \cdot SiO_2 \rightarrow 4PbO \cdot SiO_2.$$

And, finally, Yagich studied the kinetics of the reaction in which spinel forms from the oxides of zinc and aluminum, also prepared in tablet form.

It was found as a result of these investigations that:

the rate of the reactions between powdered silver sulfate (or phosphate) and magnesium oxide is subject to Equation (96) when the

latter is present in large excess, as is the reaction between tableted magnesium oxide and magnesium pyrophosphate;

the rate of reactions between tableted PbO and lead silicates, as well as those between tablets of ZnO and Al_2O_3 may be expressed by Equation (93);

the kinetics of the conversion of a polydisperse mixture of MgO with silver salts with the latter present in excess may be described by Equation (89).

Yagich reserves detailed explanations of this difference in the kinetics of the processes that he studied and their departures from the kinetics of "solid-phase" processes studied by other authors. Nevertheless, the results of his experimental studies are of great interest.

As will be seen from the above exposition, much information on the kinetics of reactions between solids is indeed full of contradictions and leaves many problems unclarified.

As was noted in References [230, 346], the chief reasons for this type of unclarity and contradiction reduced to the unjustified tendency to extend the kinetic laws prevailing under certain conditions in one stage of a reaction to the entire reaction, to reactions similar to it, and even to all so-called solid-phase processes in general.

§2. GENERAL CONSIDERATIONS

In accordance with the above, the process of physicochemical change in a solid mixture may consist of several simple physical and chemical "elementary" processes (phenomena, stages) of movement by particles of the material and changes in its structure, physical state and chemical composition.

Among these phenomena (stages), chemical reaction, diffusion, sublimation or evaporation, fusion, crystallization and certain others

- 247 -

may be of essential importance.

The rate of each such stage may, in the majority of practical cases, be expressed as a rather simple function of the relationship between the motive force of the process and the resistance to it during this stage:

$$\frac{dG_1}{d\tau} = F_1 \frac{\Delta C_1}{W_1}.$$ (98)

$$\frac{dG_2}{d\tau} = F_2 \frac{\Delta C_2}{W_2}.$$ (98a)

$$. \cdot . \quad . \quad . \quad . \quad . \quad .$$

$$\frac{dG_n}{d\tau} = F_n \frac{\Delta C_n}{W_n}.$$ (98b)

where G_1, G_2..., G_n are the degrees of conversion of the material in the first, second and later stages, respectively, τ is the time, F_1, F_2..., F_n are the areas of the contact surfaces between the phases in the first, second and later stages, respectively, W_1, W_2..., W_n are the resistances to the stages and ΔC_1, ΔC_2..., ΔC_n are the motive forces of the stages expressed in terms of the concentration drop of one of the reagents on various segments of its path toward the other reagent.

The process as a whole takes place, in general form, under extremely complex conditions capable of variation over the widest imaginable range.

First of all, one of the phenomena listed above serves as a mandatory part of each reaction in a mixture of solids, while the others take essential roles in the majority of such reactions, while still others may or may not, with equal probability, take place at all (see page 161). Further, the initial reagents may be represented in the form of anisotropic solids. The shape and size of the initial-reagent grains may be widely variable. The proportions between them in the initial mixture may vary over a wide range. Mass transfer may be ac-

complished during the reaction by motion of particles of only one re-
agent or particles of both reagents.

When two pure reagents react with one another, we may distinguish
one, or two, or several intermediate layers arising in the reaction
process, depending on conditions. If, for example, the rate of such a
reaction is restricted simultaneously by the rates of sublimation of
reagent A, the rate of its diffusion toward reagent B, and the reac-
tion between them, we have the following layers:

1) solid reagent A;

2) a gaseous phase consisting of an inert gas I and sublimated
A, the medium in which the process takes place;

3) the reaction product AB;

4) the product AB + unreacted reagent B;

5) reagent B.

During such a process, the values of the motive forces and re-
sistances associated with the stages forming this process also vary
over a wide range and in a rather complex manner, as do the areas of
the reaction surface. To form an impression of the complexity of the
relationships that arise here, it is sufficient to note that the
diffusion rate varies as a result of the progressive change in the
cross-sectional area and the thickness of the diffusion layer during
the reaction process. If a corresponding change in the rate of the
reaction proper does not take place when this happens, the process
obviously becomes nonsteady. Otherwise, obviously, the concentration
of reagent A will change at the product AB/(AB + B) interface and in
the bulk (AB + B). If the initial reagents contain significant quan-
tities of impurities or counterdiffusion of both reagents through
their reaction product occurs, the picture becomes further compli-
cated.

In view of the above, description of the kinetics of a process

in its general form by some generalizing equation becomes an extremely complex problem and can hardly result in any useful solution without sweeping simplifications that reduce the sense of the generalization to naught. Hence it is usually expedient at the very outset to restrict the problem by the following simple conditions, which are most frequently encountered in practical accomplishment of reactions in mixtures of solids:

1) the possible anisotropy of the components of the reaction mixture has no essential effect on the kinetics of the process;

2) the grain shapes of both reagents are close to regular; the grains of each reagent may be regarded as having practically the same size as a result of classification;

3) the rate of the process is not limited by the rate of heat exchange between the reacting substances and the medium surrounding them and, accordingly, is independent of the rate of melting or crystallization;*

4) by virtue of a large difference between the mobilities of the reagent particles, it may be assumed that mass transfer is accomplished by movement of the particles of only one reagent;

5) in the course of a relatively short time from the start of the reaction, there is a layer of reaction product AB that is sharply demarcated from the other layers and by comparison with which the layer of (AB + B) has a negligibly small thickness;

6) the process may be regarded as quasistationary, since at any moment it is self-regulating when the rate of all of the stages composing it depends on the rate of the slowest of them).

Solution of a problem limited by these conditions nevertheless remains quite complex and can be carried out only approximately with certain further simplifications. The results of such solution naturally

depend on the nature of these simplifications (or assumptions) or, in other words, on the approach to the problem.

Let us investigate one of these methods [346].

We note that the motive force of the reaction itself is proportional in general to the product of certain powers of the concentrations of the reagents A and B at the surface at which they interact:

$$\Delta C \sim (C_A)^m (C_B)^n.$$

If the process takes place by diffusion of reagent A through a growing layer of product AB toward the surface of reagent B (with a thickness of the AB + B layer nearly zero), the concentration of the latter at the reaction surface may be regarded as constant. We may accordingly write

$$\frac{dG}{dt} = K'(C_A)^m F,$$
(99)

where K is a constant coefficient that incorporates the concentration of reagent B at the B-AB interface.

For an extremely large number of reactions, m = 1. Given sufficient purity of B, the value of its molar concentration at the B-AB interface may be regarded as equal to 1. Then the motive force of the reaction proper (a reaction of the first order with F = const) will be expressed by the value of the concentration C_a of reagent A at the B-AB interface:

$$\Delta C = C_A.$$

It follows from Equations (98)-(98b) that

$$\Delta C_1 = \frac{dG_1}{dt} \frac{W_1}{F_1},$$
(100)

$$\Delta C_2 = \frac{dG_2}{dt} \frac{W_2}{F_2},$$
(100a)

$$\cdots \cdots \cdots \cdots$$

$$\Delta C_n = \frac{dG_n}{dt} \frac{W_n}{F_n}.$$
(100b)

The condition of the quasistationary process may be written in

the form of the expression

$$\frac{dG_1}{d\tau} = \frac{dG_2}{d\tau} = \ldots = \frac{dG_l}{d\tau} = \ldots = \frac{dG}{d\tau}, \qquad (101)$$

which indicates that in the course of each given infinitesimal time period taken at various stages of the process, the same quantity of material undergoes transformation (the values of dG/dt are naturally different for different G).

On adding Equations (100-100b), we obtain an expression for the motive force of the entire process, which consists of n stages:

$$\Delta C = \frac{dG}{d\tau} \sum_1^n \frac{W_i}{F_i}. \qquad (102)$$

From this, the approximate rate of this process will be

$$\frac{dG}{d\tau} = \frac{\Delta C}{\sum \frac{W_i}{F_i}} = \frac{\Delta C}{A_1 + A_2 + \ldots + A_i + \ldots + A_n}. \qquad (103)$$

Obviously, if any of the quantities A_1, A_2 and so forth is incommensurately smaller than other quantities of this series, then these incommensurately smaller quantities can be excluded from Equation (103) without incurring any essential error.

§3. PROCESSES LIMITING THE RATE OF CHEMICAL REACTION (THE FIELD OF CHEMICAL KINETICS)

Under conditions in which physical phenomena (such as internal diffusion, sublimation, etc.) have virtually no effect on the rate of the conversion process of the solids, this rate may be limited by the rate of any of the following chemical phenomena.

1) a first-order reaction;

2) a second-order reaction;

3) a reaction at constant concentration of the reagents, as well as a zeroth-order reaction;

4) an autocatalytic reaction;

5) several successive reactions.

For a homogeneous medium, the kinetics of these phenomena are described, as we know, by the following respective equations:

$$\frac{dy}{dt} = K(a - y),$$ (104)

$$\frac{dy}{dt} = K(a - y)(b - y),$$ (105)

$$\frac{dy}{dt} = K,$$ (96)

$$\frac{dy}{dt} = Ky(a - y)$$ (106)

(for an autocatalytic reaction of the first order),

$$\frac{dy}{dt} = K_2 a e^{-K_1 t}(1 - e^{-K_1 t})$$ (107)

(for two successive first-order reactions),

where a and b are the initial quantities of the reagents per unit volume, y is the quantity of reagents (in the same unit volume) that have been converted by the point in time τ, and K, K_1 and K_2 are constants that depend on the properties of the reagents and the conditions of the process.

The applicability of Equations (96) and (104-107) to express directly the kinetics of various conversion processes in mixtures of solids is severely restricted and in many cases impossible.

Primarily, this is a matter of the fact that all of these equations, which were derived for homogeneous reactions, can be valid for reactions taking place in heterogeneous systems only when the contact-surface area between the reagents is constant. On the other hand, continuous changes (reduction) of the contact area between the reagents takes place in reactions that occur in mixtures of crystalline solids.

For this reason, it would be more correct to write the following for a process in a solid mixture in the case, for example, of a "first-order" reaction:

$$\frac{dy}{dt} = KF(a - y)$$

where F is the contact surface between the reagents.

As we know, the grain shape of real powdered substances may be variable. In practice, however, these grains may be regarded in the majority of cases as spherical or cubic without incurring any essential error. In the analysis to follow, which was published previously in Reference [346], we shall regard them as being also approximately equal in size.

In this case, given an initial average value R of the radius or half-edge of the grain and a thickness $\underline{x}$ of the spherical or, respectively, cubic layer on these grains that has been converted into the product, the extent G of their conversion may be expressed as follows in fractions of unity:

$$G = \frac{R^3 - (R-x)^3}{R^3}.\qquad(108)$$

From this, the value of the radius or half-edge of the unreacted part of the grain after a certain time has elapsed since the beginning of the reaction will be

$$R - x = R(1-G)^{\frac{1}{3}}.\qquad(109)$$

In accordance with this, the dependence of the reaction-surface area of a spherical or cubic grain on the extent of conversion will take the form

$$F = A(1-G)^{\frac{2}{3}},\qquad(110)$$

where G is the extent to which the material whose surface limits the rate of the process is converted and

$$A = 4\pi R^2 \text{ (sphere) or } A = 24R^2 \text{ (cube)}$$

To this we must add that the possibility of generalizing description of the kinetics of autocatalytic reactions in solid mixtures by Equation (97) is obviously excluded, because it can apply only for a definite, invariably quite improbable combination of conditions (rate

of reaction does not depend on concentration of reagents and contact surface between them and is zero at the beginning of the process, when y = 0).

A more general expression for the rate of such reactions would obviously be the equation

$$\frac{dy}{dt} = K(B + y^n)(a - y)^r.$$ (111)

which, with B = 0 and m = n = 1, i.e., only in a single particular case, can be transformed into Equation (106).

However, even this equation is in a position to describe the kinetics of autocatalytic reactions in solids only in a highly general and approximate form (see §2 of this chapter).

In the general case, the rate of the heterogeneous interaction between the two substances, which is what limits the reaction proper, can be expressed by the equation

$$\frac{dQ}{dt} = KC_1^n C_2^a F.$$ (112)

which, for a second-order reaction, assumes the form

$$\frac{dQ}{dt} = KC_1 C_2 F.$$ (113)

where C_1 and C_2 are the respective concentrations of the first and second reagents at the interaction surface, F is the area of this surface and K is a constant that characterizes the properties of the reagents and the conditions of the process.

Depending on the mechanism and conditions of a reaction between two substances, the concentration of each of them at the surface of contact and the area of contact may remain practically constant or vary essentially during the course of the reaction. Accordingly, the dependence of the process rate on degree of conversion of the initial substances may take a wide variety of forms. Thus, if the concentration of the two reagents does not change during the course of the

reaction, then obviously with a constant contact area between the reagents (tablet reaction), the rate of the process may be expressed by Equation (96), while if the contact area changes, as it does in a powdered mixture,

$$\frac{dG}{dt} = K(1-G)^{\frac{2}{3}}.$$ (114)

In the case, for example, of a direct, reaction-rate-limiting reaction between two solids in accordance with the scheme

$$A_\tau + B_\tau \rightarrow AB_\eta$$

or a solid and a liquid according to the scheme

$$A_\tau + B_\varkappa \rightarrow AB_\eta$$

or a solid and a gas formed by sublimation, according to the scheme

$$A_\tau \rightarrow A_\tau$$
$$A_\tau + B_\tau \rightarrow AB_\eta$$
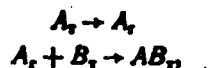
the concentration of the two reagents at the surface of contact between them remains constant over the course of the reaction.

Here, Equation (114) will obviously be in force for a powdered mixture of reagents consisting of spherical or cubic grains.

Let us consider a process having a different mechanism. Suppose that the concentration of one of the reagents at the surface of contact between them changes continuously, while that of the second remains constant during the course of the reaction. It is easily seen that such conditions might occur in reality.

Thus, in the case of interaction in a mixture of reagents with participation of a liquid phase, in accordance with the scheme

$$A_\tau \rightarrow A_{\varkappa},$$
$$A_\varkappa + B_\tau \rightarrow AB_\eta$$
$$AB_\tau + A_\varkappa \rightarrow (AB + A)_\varkappa \quad \text{etc.}$$
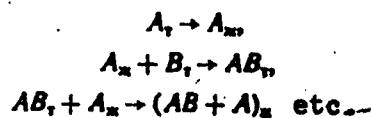
the concentration of reagent B at the B–(AB + A) interface is constant, while the concentration of A, which depends on the quantity of AB present in the reaction mixture, is a function of degree of conversion:

- 256 -

$$C_1 = \text{const,}$$
$$C_2 = K(1 - \alpha G),$$

where G and αG are, respectively, the degrees of conversion of substances B and A and $\alpha = n/m$ is the composition coefficient of the mixture, if n is the stoichiometric reaction coefficient, which expresses the number of moles of reagent A reacting with one mole of reagent B, and m is the molar ratio between the quantities of A and B in the initial mixture.

Here, the rate of the reaction

$$\frac{dG}{d\tau} = K C_2 F = K''(1-G)^{\frac{2}{3}}(1 - \alpha G), \tag{115}$$

where $\alpha G < 1$.

The rather complex solution of Equation (115) leads to the equation

$$\ln \frac{1 + \Delta^{\frac{1}{3}}(1-G)^{\frac{1}{3}}}{\sqrt{\Delta^{\frac{2}{3}}(1-G)^{\frac{2}{3}} - \Delta^{\frac{1}{3}}(1-G)^{\frac{1}{3}} + 1}} + 1,75 \, \text{arc tg}[1,17\Delta^{\frac{1}{3}} \times$$
$$\times (1-G)^{\frac{1}{3}} - 1] - \ln \frac{1 + \Delta^{\frac{1}{3}}}{\sqrt{\Delta^{\frac{2}{3}} - \Delta^{\frac{1}{3}} + 1}} -$$
$$- 1,75 \, \text{arc tg} \, 1,17(\Delta^{\frac{1}{3}} - 1) = K\tau, \tag{116}$$

where $\Delta = \frac{\alpha}{1 - \alpha} = \frac{n}{m - n}$.

With stoichiometric composition of the mixture (i.e., when $n = m$ and $\alpha = 1$), Equation (115) assumes the form

$$\frac{dG}{d\tau} = K'(1-G)^{\frac{5}{3}}. \tag{117}$$

If the products of such a reaction accelerate it (autocatalytic reaction), its rate equation assumes the form

$$\frac{dG}{d\tau} = K(B + G^n)(1-G)^{\frac{5}{3}}. \tag{118}$$

It is necessary to dwell briefly on derivation of the kinetic equation of successive reactions in mixtures of solids.

We may imagine a series of combinations of successive reactions of the same or different orders. However, to characterize briefly our reasoning applied to these reactions, it will be sufficient to limit ourselves to consideration of one such combination.

Suppose that the conversion proceeds in accordance with the last scheme (page 256).

$$[A_\tau \to A_{II}; \quad A_{II} + B_\tau \to AB_1; \quad AB_1 + A_{II} \to (AB + A)_{III}] \quad \text{etc.}$$

and consists of the two successive reactions

1. I → II and 2. II → III,

whose rates, which conform to Equation (117) are commensurate with one another. Then, in accordance with Equation (117),

$$\frac{dG'}{d\tau} = K_1 (1 - G')^{\frac{2}{3}} \tag{117a}$$

and

$$\frac{dG''}{d\tau} = K_2 [G'(1 - G'')]^{\frac{2}{3}}. \tag{117b}$$

where G' and G" are the degrees of conversion of I to II and II to III, respectively (in fractions of unity), and K_1 and K_2 are constants characterizing the rates of the first and second reactions, respectively. Integrating Equation (117a), we obtain

$$G' = 1 - (1 + K_1'\tau)^{-\frac{3}{2}}. \tag{119}$$

In analogy to Equation (117a), we may write

$$G'' = 1 - (1 + K_2'\tau)^{-\frac{3}{2}}. \tag{120}$$

Substitution of Equations (119) and (120) into Expression (117b) gives

$$\frac{dG''}{d\tau} = K_2 [(1 + K_2'\tau)^{-\frac{3}{2}}[1 - (1 + K_1'\tau)^{-\frac{3}{2}}]]^{\frac{2}{3}}. \tag{121}$$

In this case, the over-all degree of conversion of initial substance I into the final product III is

$$G = G'G''. \tag{122}$$

where G' and G" are determined from Equations (119) and (120).

To this we should add that in the particular case of successive reactions in which their rates are not commensurate with one another, the over-all rate and kinetic laws of the process, which is limited by chemical effects, are determined respectively by the rate and kinetics of the slowest reaction and can be expressed, for example, by one of Equations (114-118).

Finally, the case of change in the concentrations of both reagents at the reaction surface with a simultaneous change in the latter's area is also possible.

If in this case the degrees of conversion of each of the two reagents into the product, expressed in fractions of unity, amount respectively to G and G_1 and the surface area of the first of them, which is converted by the fraction G of unity (as might occur when the change in the area of the first reagent in the course of the process is considerable, while that of the second is quite negligible), is the factor limiting the rate of the process, then the rate of the reaction in a mixture consisting of spherical or cubic grains may be expressed by the equation

$$\frac{dG}{dt} = K(1-G)^{\frac{1}{3}}(1-G_1).$$

(123)

The value of the coefficient K in Equations (114-118) and (123) depends on the initial concentration of the reacting substances. Since the factor limiting the rate of the process is the area of the reagent converted by a fraction G of unity, it is obvious that $G > G_1$ given identical grain sizes and densities in the reagents.

When the proportions of the reagents in the system and in the stoichiometric equation of the reaction are such that $G_1 \rightarrow 0$ at a sufficiently large value of G, Equation (123) is naturally converted

into Equation (117).

A highly essential point is that when $G \ll 1$ or, in other words, when $G \to 0$ (and, accordingly, $G_1 \to 0$), each of Equations (114, 115, 117, 118) and (100) assumes the form of Equation (96), i.e., that the rate of all reactions is practically constant under these conditions.

The function $(1 - G)$ in Equations (114)-(118) and (123) characterizes the concentration C_{sr} of the reacting substance in bulk, while the rate of the heterogeneous reaction between the two substances in the field of chemical kinetics is, strictly speaking, a function of the concentration C_1 of one of them at the surface of the particles of the other:

$$\frac{dG}{dt} = f(C_1).$$
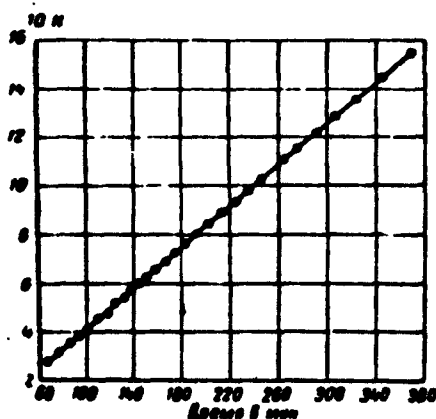
Fig. 57. Kinetics of reaction of soda with silicon dioxide in the presence of NaCl with $[SiO_2]$: $[Na_2CO_3]$ = = 1, t = 740° and a reagent grain size r = 0.036 mm (reaction limits). 1) Time in minutes.

For the cases considered, however, in which the rate of diffusion is incommensurately higher than the rate of the reaction proper, $C_1 = C_{sr}$ and, consequently, the reaction rate may be regarded as a function of the reagent concentration in bulk.

The above enables us to judge the dependence of the rate of the limited reactions of so-called solid-phase processes on the initial grain size of the original mixture.

Thus, for a reaction accompanied by a change in the concentration of one of the reagents at the surface F on which they react and being of the first order for a constant value of the area F, we have

TABLE 24

Kinetics of Reaction of Soda With Silicon Dioxide in the Presence of NaCl* (With $[SiO_2]:[Na_2CO_3] = 1$, Reagent Grain Size r = 0.036 mm and t = 740°)

$\frac{1}{\tau}$	σ	$10 \cdot N$	$10^? \cdot K$
48	0.239	2.01	4.2
57.5	0.273	2.4	4.2
67.5	0.307	2.70	4.1
77	0.341	3.22	4.2
84.5	0.362	3.5	4.2
92	0.382	3.8	4.1
100	0.403	4.12	4.1
108	0.423	4.45	4.1
116	0.444	4.8	4.1
125	0.464	5.2	4.2
131	0.477	5.45	4.2
137.5	0.492	5.73	4.2
145	0.505	6.05	4.2
152.5	0.519	6.32	4.2
159	0.532	6.62	4.2
167.5	0.545	6.93	4.2
175.5	0.56	6.3	4.2
184	0.574	6.68	4.2
193.5	0.587	8.05	4.2
203.5	0.6	8.45	4.2
214	0.615	8.93	4.2
225	0.628	9.35	4.2
237	0.642	9.85	4.2
250	0.655	10.35	4.2
263.5	0.67	11.00	4.2
275	0.683	11.44	4.2
291	0.696	12.18	4.2
307	0.71	12.82	4.2
325	0.742	13.5	4.2
344.5	0.737	14.4	4.2
370	0.751	15.38	4.2

* Reaction limits.

1) τ, minutes.

$$\frac{d\sigma}{dt} = K'(1-\sigma)[A'(1-\sigma)^{\frac{2}{3}}], \qquad (124)$$

where $A' = 4\pi R^2$ for a single spherical grain.

The amount of the material in an ensemble of grains of initial radius R that has been converted is proportional to the product of the extent of conversion of one grain by the number of grains N in a unit weight of such a mass:

$$\frac{d\sigma}{dt} = K'(1-\sigma)^{\frac{2}{3}} A'N, \qquad (125)$$

where

$$N = \frac{1}{\frac{4}{3} \pi R^3 \gamma}. \tag{126}$$

if γ is the apparent specific gravity of the grain.

In view of this, the final rate of a reaction of this kind will be

$$\frac{d G}{d \tau} = K R^{-1} (1 - G)^{\frac{2}{3}}. \tag{127}$$

Integration of Equation (127) with the initial condition $G = 0$ and $\tau = 0$ results in the equation

$$H(G) = (1 - G)^{-\frac{1}{3}} - 1 = K R^{-1} \tau, \tag{128}$$

which enables us to characterize the rate of the process as a function of the particle radius in the initial mixture. It is readily seen that Equations (127) and (128) are also valid for cubic grains if R characterizes their average size.

Substituting $KR^{-1} = K'$ in Equation (128), we may write

$$H(G) = (1 - G)^{-\frac{1}{3}} - 1 = K' \tau. \tag{128a}$$

The validity of Equation (128a) under conditions in which the process rate is limited by the rate of the reaction itself has been confirmed experimentally by Ginstling and Fradkina [231] on the example furnished by the reaction of soda with silicon dioxide at a temperature of 740° (Table 24, Fig. 57). The diffusion resistance of the process was limited here by its taking place in a finely dispersed mixture of the reagents in the presence of sodium chloride as a flux.

It is important to note that calculation of the rate of a given process subject to any of the equations given above may give varying results, depending on the relationship between the grain sizes of the reagents.

Further, the form of the kinetic relationships changes considerably if the reaction takes place not in a powdered mixture consisting

of particles that approach the spherical or cubic more or less closely, but between reagents taking the form of tablets and in contact with one another at flat surfaces. In this case, the rate of the "solid-phase" processes, which are limited by chemical interaction, must obviously be subject to Equations (96), (104), (105), (107) and (111), although, as follows from the equations given above, $dy/d\tau \rightarrow K$ here too as $y \rightarrow 0$.

Thus, the microkinetics (the chemical kinetics proper) of different "solid-phase" reactions may assume different natures depending on the conditions under which they are run and differing from the nature of the homogeneous reactions, which, in accordance with the stoichiometric equations, are characterized by the same respective numbers of reacting molecules.

§4. PROCESSES LIMITED BY THE RATE OF FORMATION OF SEEDS

These processes are autocatalytic (page 183). Investigators have proposed various equations at various times for description of their kinetics.

L'yuis and later Tsentnershver and Bryuss and Makdonal'd and Khinshel'vud tried unsuccessfully to extend the kinetic equations of homogeneous and, in particular, homogeneous autocatalytic reactions to these processes.

Assuming that 1) the rate of a solid-phase reaction that passes through the emergence and growth of nuclei of a crystalline product is proportional to the interphase surface on which the process is localized and that 2) the area of this surface is proportional to the product of the surface areas of the initial substance and the product and, further, that $S = KV^{2/3}$ (where S is the surface area and V is the phase volume), Roginskiy and Shul'ts [269] obtained the following expression to describe the kinetics of this reaction:

$$\frac{dG}{d\tau} = KG^{\frac{1}{3}}(1-G)^{\frac{1}{3}},\qquad(129)$$

where G is the fraction of the material that has reacted.

The validity of Equation (129) was confirmed for the processes of decomposition of $KMnO_4$ [269], $CaCO_3 \cdot 6H_2O$ [349], zinc oxalate [350] and certain other substances. The fact of localization of processes of this type at an interface was thus confirmed.

It was subsequently shown by Yerofeyev [351] that Equation (129) is not universal and valid for all reactions passing through stages of formation and growth of solid-product nuclei.

To describe the kinetics of such reactions, Yerofeyev [270, 351, 352] proposed the equation

$$G = 1 - e^{-K\tau^n},\qquad(130)$$

which can also be expressed approximately in the form

$$\frac{dG}{d\tau} = KG^x(1-G)^y.\qquad(131)$$

These equations were derived on the assumption that the process in which the initial centers of the reaction arise may be multistaged, i.e., that the process of this emergence may depend on time (to the extent that the concentration of the reacting substance does not remain constant during the reaction process).

In expanded form, Equation (130) reads as follows:

$$G = 1 - e^{-\frac{\nu_0 U^n K_1 K_2 \cdots K}{(\sigma+3)!}\cdot \tau^{\sigma+3}},\qquad(130a)$$

where ν_0 is the number of potential points at which initial reaction centers may arise, σ is the number of intermediate stages in the process of initial-center formation, U is the linear rate of reaction-nucleus growth and K_1, K_2..., K are constants characterizing the kinetic orders of the intermediate stages in the formation of the initial reaction centers.

This equation was proposed as a description of the kinetics of

formation and growth of spherical nuclei. In cases where the initial centers have linear and flat shapes, Equation (130a) accordingly assumes the form

$$G = 1 - e^{-Kr^{n+2}}$$ (130b)

and

$$G = 1 - e^{-Kr^{n+1}}.$$ (130c)

Thus, according to Yerofeyev, the value of $\underline{n}$ in Equation (130) depends on the presence of initi 1 reaction centers in the body at $\tau = 0$, on the form of the nuclei, the number of intermediate stages in the process of initial-center formation, and on certain other factors; here, the value of $\underline{n}$ may vary from unity to any integer.
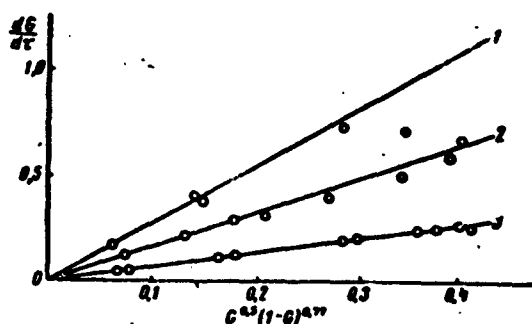
Fig. 58. Rate of conversion of NH_4NO_3 III → IV as a function of the quantity $G^{0.5}(1 - G)^{0.77}$ at temperature of 1) $34.02°$; 2) $34.55°$; 3) $35.75°$.

Equation (130) has been confirmed experimentally on the example furnished by thermal decomposition of a number of oxides and carbonates [265, 353-356], the polymorphic transformation of ammonium nitrate (Figs. 58 and 59) [352] and on certain other reactions.

However, in addition to the assumption explained above, the derivation of this equation also assumes that from the time at which the reaction nuclei merge with one another the rate of the reaction diminishes in proportion to the percentage of material that has not

- 265 -
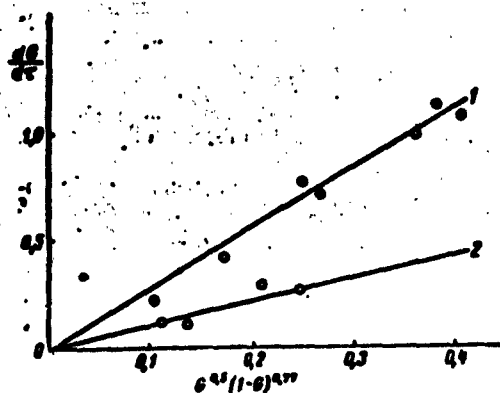
Fig. 59. Rate of conversion of NH_4NO_3 III → IV as a function of the quantity $G^{0.5} (1 - G)^{0.77}$ at temperature of 1) $30.5°$; 2) $31.1°$.

reacted. Actually, as was correctly noted by Bel'kevich [268, 357], this assumption is not always justified. The decline in reaction rate after its nuclei have intercepted one another may take place more rapidly than the decrease in the proportion of material unreacted. This would be expected particularly in those cases where the appearance of the initial centers takes place not over the entire volume of the crystal, but chiefly on certain elements of its surface. If the reaction nuclei form, for example, preferentially at the polyhedral vertices of crystals or on specific points of their surfaces, the probability that the nuclei will intercept one another increases more and more rapidly as the nuclei penetrate into the interior of the particle (grain), because interception may take place not only with nearby nuclei, but also with nuclei that have formed or. more remote surfaces of the crystal.

Essential mathematical difficulties arose in theoretical analysis of the kinetics of reactions of this type, so that only isolated particular cases pertaining to this analysis — usually the beginning or end of the process — were treated in the studies by Bredli, Kolvin and Yum [358], Roginskiy [269, 359], Izmaylov [360] and Yerofeyev [270, 351, 352, 361].

The most general and rigorous solution of the problem was given in the reports by Todes and Bogutskiy [362] and Todes [363, 364]. Applying special probability methods, these investigators considered

- 266 -

(taking into account the intersections of the reaction zones as they move forward) the propagation, by a topochemical reaction of the type described, of particles of limited size and regular (spherical) and arbitrary shape into the interior of a particle of infinitely large dimensions (the curvature of which may be disregarded)..

The differential expressions obtained as a result for reaction rate are not integrated in their final form. Nevertheless, these studies resulted in important conclusions as to the kinetics of the reactions considered.

The authors showed, among other things, that in the general case the rate of such reactions passes through a maximum during their progress. The position and magnitude of the maximum were found for the "plane" case. The rapidity with which this maximum was attained and the rapidity of the subsequent drop in reaction rate was established for spherical particles as a function of the parameter ω, which expresses the ratio of the average time necessary for a reaction zone proceeding from one initial center to reach the nearest initial center to the time taken by the reaction in advancing from the surface to the geometrical center of the particle (Fig. 60). It was shown that with $\omega < 0.001$, the rate of conversion attained its maximum almost instantaneously after onset of the reaction, at a negligibly small degree of conversion of the initial material. In this case, the zones of conversion from the various initial reaction centers fuse at the very beginning and form a unified, practically spherical front that presses on uniformly into the interior of the particle. With $\omega = 1$, no single front forms at all, since the conversion zones from the individual initial centers may "overgrow" the entire particle before formation of the next center on the remaining free surface.

Figure 61 shows the position of the rate maximum (with respect to
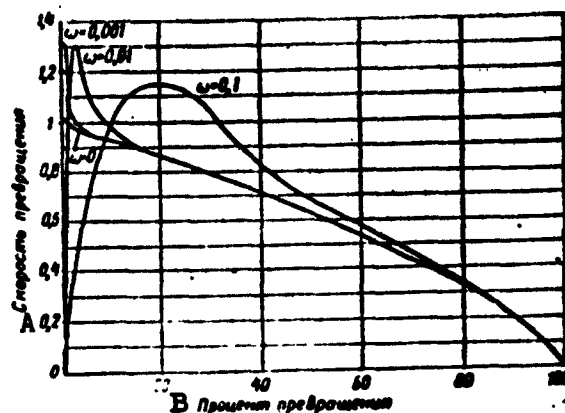
Fig. 60. Kinetics of reaction proceeding via formation of initial centers. Propagation of reaction in spherical particle. A) Rate of conversion; B) percent conversion.
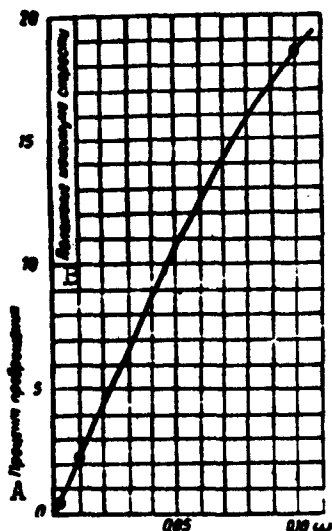
Fig. 61. Position of reaction-rate maximum for reaction proceeding through formation of initial centers for various degrees of conversion as a function of ω. A) Percent conversion; B) position of rate maximum.

degree of conversion) as a function of ω.

Todes [364] showed that the nature of the kinetic curves depends only slightly on the grain shape of the initial material, but is determined essentially by its grain sizes. In the case of continuous formation of conversion centers at the particle surface, an optimum of conversion rate with respect to particle refinement should exist. Otherwise, when the initial centers arise at the particle surface before the process begins, we should observe incomplete conversion to a greater extent as the particle size became smaller.

It is interesting to note that almost simultaneously with Todes and Bogutskiy,

Mampel' [365] arrived by a somewhat different route at results similar

- 268 -

to those obtained in References [362, 363].*

According to Bel'kevich, it may be assumed in connection with the remark made earlier (page 265) that the rate of a reaction of the type under consideration drops off as a result of intersection of nuclei in direct proportion to the quantity $(1 - G)^S$, where $s > 1$.

Thus, Bel'kevich [268, 357] obtained the equation

$$\frac{1}{(1-G)^\mu} - 1 = K\tau^n,$$

(132)

where $\mu = S - 1$.

Experimental investigation of the thermal decomposition of cadmium and magnesium carbonates and the oxalates of silver, lead and nickel, as well as certain other substances, showed the inadequacy of Equation (130) and the validity of Equation (132) for these processes (Figs. 62 and 63). Here, the value of the quantity S, the physical significance of which has not as yet been figured out, varied from 2 to 5 as a function of the specific reaction involved.

The rate of a reaction subject to Equation (132) is expressed as follows:

$$\frac{dG}{dt} = \frac{nK^{\frac{1}{n}}}{\mu}(1 - G)^{\mu+1}[(1 - G)^{-\mu} - 1]^{1 - \frac{1}{n}}.$$

(133)

It follows from Equation (133) that this rate is zero for both $G = 0$ and $G = 1$, i.e., it passes through a maximum. This maximum, the presence of which has been confirmed experimentally (Fig. 64 [366]), occurs theoretically at

$$\tau_m = \left[\frac{(n-1)\mu}{(n+\mu)K}\right]^{\frac{1}{n}}.$$

(134)

The maximum rate here is

- 269 -

$$\left(\frac{dG}{dt}\right)_{max} = \frac{(n-1)^{1-\frac{1}{n}}(n+\mu)^{\left(\frac{1}{n}+\frac{1}{\mu}\right)}K^{\frac{1}{\mu}}}{n^{\frac{1}{\mu}}\mu^{\frac{1}{n}}(\mu+1)^{1+\frac{1}{\mu}}}.$$ (135)

On the other hand, the rate value is proportional to the interface area between the initial and final solid phases:

$$\frac{dG}{dt} = \varphi F$$

or

$$F = \varphi^{-1}\frac{dG}{dt}.$$ (136)

where φ^{-1} is the rate referred to a unit interface area and F is the size of this entire area.
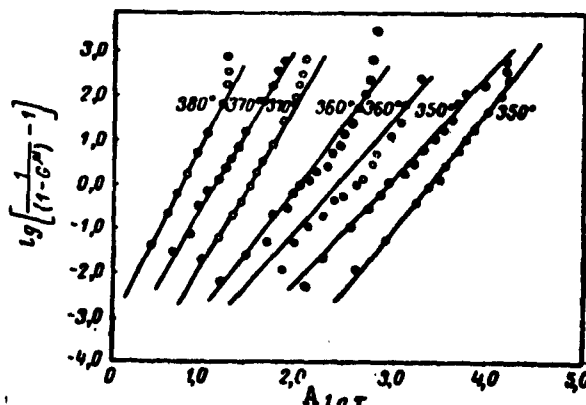
Fig. 62. Kinetics of thermal decomposition of magnesium carbonate at various temperatures (diagram arbitrarily condensed). A) log τ.

If we now compare Equations (133) and (136), we may conclude [366] that in reactions proceeding via formation and growth of nuclei of a solid product, the size of the interface area must also pass through a maximum (Fig. 65).

It has not as yet been possible to confirm this statement experimentally by any type of direct measurement.
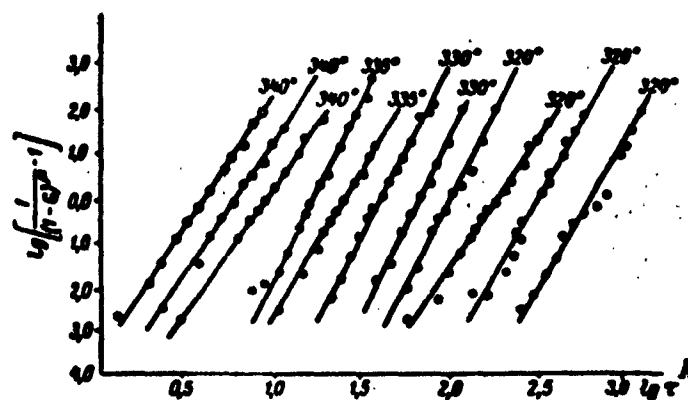
Fig. 63. Kinetics of thermal decomposition of lead oxalate at various temperatures (diagram arbitrarily condensed). A) log τ.
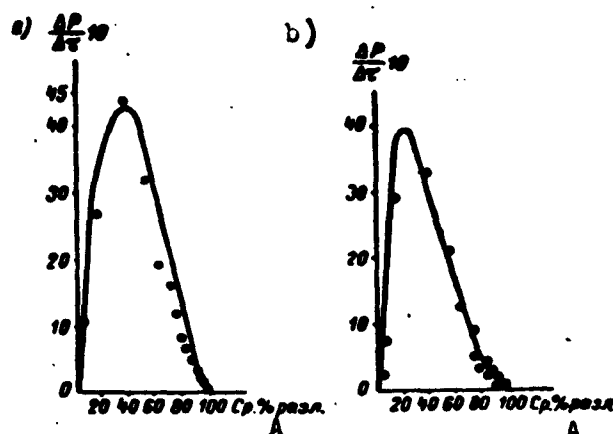
Fig. 64. Kinetics of thermal decomposition of a) $MgCO_3 \cdot 3H_2O$; b) $MgCO_3 \cdot 4H_2O$. Curves computed from Equation (132) and experimental points. A) Average % decomposed.
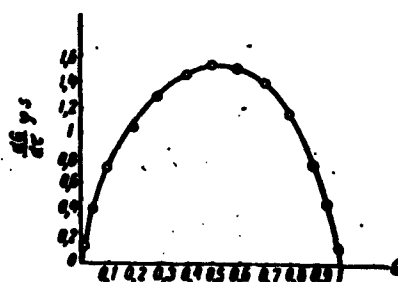
Fig. 65. Change in interface area during thermal decomposition of a crystalline solid.

- 271 -

§5. PROCESSES LIMITED BY THE RATE OF DIFFUSION (DIFFUSION REGION)

The rate of the majority of reactions between solids is limited by diffusion of the reagent through a layer of product.

In the general type of these reactions, a substance A reacts with a substance B to form a product AB (Fig. 66) the thickness of whose layer increases continuously during the course of the process. Here, substance A (or a product of its decomposition) diffuses toward the surface of substance B through a layer of product AB at a rate that is immeasurably lower than the rate of the chemical reaction between substances A and B, so that diffusion determines the kinetics of the process completely.
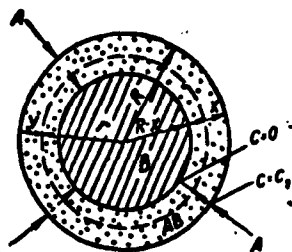
Fig. 66. Diagram of process limited by rate of internal diffusion.

Since the external resistance to diffusion is considerably smaller than the diffusion resistance of the product AB, the concentration of substance A in the surface separating it from AB is practically constant. At the surface separating AB and B, the concentration of substance A is constant at zero due to the very high (as compared with the diffusion rate) rate of the chemical reaction of A with B.

As was indicated earlier, Yander, investigating the kinetics of the type of reaction described, proceeded from the Fik differential equation for the rate of diffusion through a flat diffusion layer. Having thus derived Equations (91) and (93), Yander extended them to reactions in powdered mixtures consisting of spherical, cubic and similar "bulky" particles.

It is obvious, however, that these equations can be applied to spherical, cubic and similar particles only at small values of x/R, where $\underline{x}$ is the thickness of the diffusion layer of the product AB and

R is the initial grain radius of the "coated" reagent, i.e., only in cases where the degree of conversion of substance B into the product is small. The overwhelming majority of Yander's experimental data pertain to precisely this case.

With high degrees of conversion of substance B and, accordingly, large x/R, Equations (91) and (93), which were derived for the "plane" case, are inapplicable to the case, for example, of a sphere.

As a result of this, and because the relationships derived by Yander have been widely used in applications to the widest range of degrees of conversion, it was expedient to derive corresponding relationships for spherical grains. This problem was solved by Ginstling and Braunstein [367].

To examine this problem, let us introduce the additional symbols:

C — the concentration of substance A in the layer of product AB;

C_1 — the concentration of A at the A-AB interface;

D — the diffusion coefficient of A in AB;

r — the distance from the A-AB interface to a certain arbitrary spherical surface in the direction of diffusion;

$\varepsilon = \rho n^*/\mu$ — a proportionality coefficient (here ρ is the specific gravity and μ the molecular weight of AB; $\underline{n}$ is the stoichiometric coefficient of the reaction, which expresses the number of moles of substance A that react with one mole of B).

By virtue of spherical symmetry, the concentration C of substance A in the product layer AB is a function only of the distance $\underline{r}$ from the center of the sphere. $C(r)$ may be found by solution of the Fik equation, which takes the form of Expression (32) for the case of spherical symmetry and in spherical coordinates.

In the case under consideration, the boundary and initial conditions may be formulated in the form

$$C(r)\Big|\begin{matrix}-C_1\\ r\big|=R\\ \tau\big|>0,\end{matrix} \qquad (137)$$

$$C(r)\Big|\begin{matrix}=0\\ r\big|=R-x,\end{matrix} \qquad (138)$$

$$-\frac{dx}{d\tau}=\frac{D}{\iota}\left(\frac{\partial C}{\partial r}\right)_{r=R-x}. \qquad (139)$$

$$x\Big|\begin{matrix}=0\\ \tau\big|=0.\end{matrix} \qquad (140)$$

We shall regard the process as stationary if at a given $\underline{x}$ a given constant quantity of substance A diffuses per unit time through any cross section of the layer of product AB. Obviously, when this condition is not observed, the process will be nonstationary.

Accordingly, we shall distinguish between the "stationary" and "nonstationary" problems.

It has been shown [367] that in the case of diffusion through a plane layer, the solution of the "nonstationary" problem

$$\frac{\partial C}{\partial \tau}=D\frac{\partial^2 C}{\partial y^2}$$

for boundary and initial conditions similar to conditions (137)-(140) results in the same Equation (91) as does solution of the equation analogous to (138) for the "stationary" problem, in which the concentration of substance A at the interface between A and AB has a certain value C_1' instead of C_1.

Let us assume that in the case of diffusion through a spherical layer, we have a similar result, i.e., that solution for the nonstationary "spherical" case may reduce to solution of the equivalent "stationary" problem.

Let us denote the concentration of substance A at the surface of the sphere in the equivalent problem by C_1' and the quantity of substance A that diffuses per unit time through any cross section of the product layer AB by $M(x)$ (remembering that $M(x)$ is different for different $\underline{x}$).

For a given constant x and variable r we have

$$D \frac{\partial C}{\partial r} 4\pi r^2 = M(x) = \text{const},$$

from which

$$\frac{\partial C}{\partial r} = \frac{M(x)}{4\pi r^2 D}. \tag{141}$$

Let us now determine $M(x)$. Integrating Equation (141) between the limits $r = R - x$ and $r = R$, we shall have

$$C_1' = - \frac{M(r)}{4\pi D} \frac{1}{r} \Big|_{R-x}^{R} = \frac{M(x)}{4\pi D} \frac{x}{R(R-x)}.$$

from which

$$M(x) = \frac{C_1' R(R-x)4\pi D}{x}. \tag{142}$$

Substituting Expression (142) in Equation (141), we shall have

$$\frac{\partial C}{\partial r} = \frac{C_1' R(R-x)}{x r^2}. \tag{143}$$

and, substituting Equation (143) into Equation (139), we obtain an equation that expresses the rate of thickening of the product layer AB in a spherical particle:

$$\frac{dx}{d\tau} = K_1 \frac{R}{x(R-x)}. \tag{144}$$

where

$$K_1 = \frac{D}{\epsilon} C_1'.$$

Integrating Expression (144) with application of the initial condition (140) results in the equation

$$x^2 \left(1 - \frac{2}{3} \frac{x}{R}\right) = K'\tau, \tag{145}$$

where

$$K' = 2K_1.$$

Obviously, when $x \ll R$, Equation (145) turns into (91), so that

$$K' = K^2.$$

To determine K, we introduce the notation

$$Z = \frac{K}{2\sqrt{D}}.$$

As was shown in the above-mentioned Reference [367], we may, by transforming the familiar equations of Vulis [77], obtain the following expression for calculation of Z:

$$2 \frac{\epsilon}{C_1} Z = \frac{\Phi'(Z)}{\Phi(Z)}.$$ (146)

where Φ is the error-integral symbol.

With $\epsilon/C_1 > 7.5$, we may, with a certain degree of accuracy, use the expression

$$Z \simeq \sqrt{\frac{C_1}{2\epsilon}}.$$ (147)

and, if $\epsilon/C_1 < 0.17$, the approximate equation

$$Z \simeq \sqrt{\ln \frac{C_1}{\epsilon} - 0.57}.$$ (148)

For $7.5 > \epsilon/C_1 > 0.17$, the values of Z are determined from the curve of Fig. 67, which corresponds to Equation (146).

Knowing the values of ϵ and C_1 for a given process, we may employ the above expressions and diagram to compute values of the constant K from the known value of the diffusion coefficient D or, conversely, the value of D from an experimental value of K.

It is interesting to determine the change in rate $dx/d\tau$ of thickening of the product layer AB as a function of the ratio x/R.

Designating $x/R = i$, we have from Equation (144)

$$\frac{dx}{d\tau} = \frac{K_1}{i(1-i)}.$$ (149)

As was shown earlier [367], $dx/d\tau$ has a minimum at $i = 0.5$, i.e., at $x = R/2$. Yesin and Gel'd [368] drew attention to this fact.

The data presented below characterize the rate of thickening of the product layer as a function of the ratio x/R.
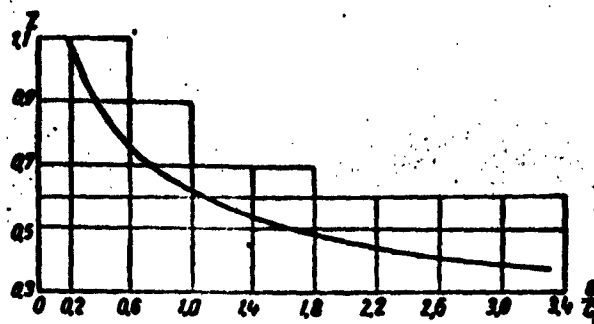
Fig. 67. Z as a function of the ratio ε/C_1 [according to Equation (146)].

i	0	0,05	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	0,95	1
$\dfrac{1}{K_1}\dfrac{dx}{d\tau} = \dfrac{1}{i(1-i)}$	∞	21,2	11,1	6,25	4,76	4,16	4,0	4,16	4,76	6,25	11,1	21,2	∞

The quantity $(1/K)(dx/d\tau)$ is also shown in Fig. 68 as a function of i.

It will be seen from the diagram that the rate $dx/d\tau$ of thickening of the layer of product AB diminishes continuously as the quantity x/R varies from 0 to 0.5 and then rises symmetrically from the minimum to infinity as x/R varies from 0.5 to 1.

In estimating the rate of the process, it is only necessary to remember that at the limiting values of i, i.e., when $x/R \to 0$ and $x/R \to 1$, the rate of thickening of the product AB layer is not infinite, since in these cases the value of $dx/d\tau$ is determined by the rate of the chemical reaction and not by diffusion.

The equations derived express the thickness of the product layer as a function of time.

In practice, it is of considerably greater interest to derive equations for calculation of the degree of conversion of the material.

For this purpose, let us express the thickness of the product layer in terms of the degree of conversion G of the "coated" reagent.
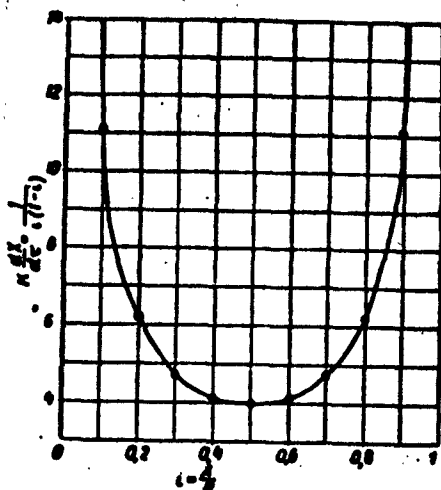
Fig. 68. Rate of thickening of product layer as a function of the ratio x/R.

We have from Equation (103)

$$x = R(1 - \sqrt[3]{1-G}). \qquad (150)$$

Substituting Expression (150) into (145), we obtain an equation expressing the extent of conversion as a function of process time and particle radius:

$$I(G) = 1 - \frac{2}{3} G - (1-G)^{\frac{2}{3}}$$

$$= \frac{K^2 \tau}{R^2} = K' \tau. \qquad (151)$$

If, after Yander, we substituted Equation (150) into Expression (93), we should have

$$I_s(G) = 1 + (1-G)^{\frac{2}{3}} - 2(1-G)^{\frac{1}{3}} = \frac{K_s^2 \tau}{R^2} = K'_s \tau. \qquad (152)$$

Substituting Formula (150) into Expression (144), we obtain an equation for the conversion rate:

$$\frac{dG}{d\tau} = \frac{3K^2}{2R^2} \frac{(1-G)^{\frac{1}{3}}}{1-(1-G)^{\frac{1}{3}}}. \qquad (153)$$

to which we may impart the form

$$\frac{dG}{d\tau} = K' \frac{(1-G)^{\frac{1}{3}}}{1-(1-G)^{\frac{1}{3}}}. \qquad (153a)$$

According to Yander, the rate of conversion would be determined by the formula

$$\frac{dG}{d\tau} = \frac{3K^2}{2R^2} \frac{(1-G)^{\frac{2}{3}}}{1-(1-G)^{\frac{1}{3}}} \qquad (154)$$

or

$$\frac{dG}{d\tau} = K' \frac{(1-G)^{\frac{2}{3}}}{1-(1-G)^{\frac{1}{3}}}. \qquad (154a)$$
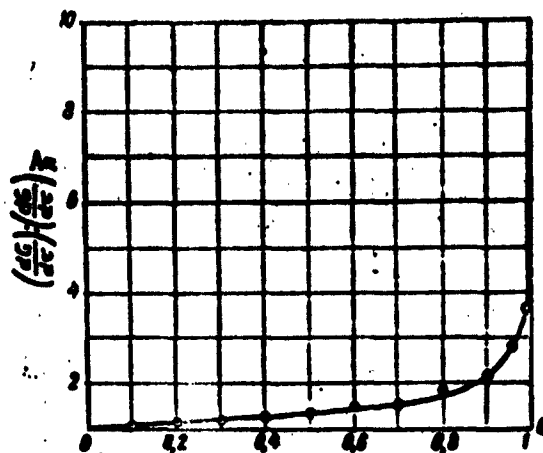
Fig. 69. Ratio of process rates computed from Equations (153) and (154) as a function of G. A) Ya [Yander].

TABLE 25

Relationship Between Process Rates Computed By Equations (153) and (154) With Equal Values of G

a	$1-a$	$(1-a)^{\frac{1}{3}}$	$\left(\frac{dQ}{d\tau}\right)_s : \left(\frac{dQ}{d\tau}\right)_s = (1-a)^{-\frac{1}{3}}$
0,1	0,9	0,9655	1,045
0,15	0,85	0,9473	1,055
0,2	0,8	0,9283	1,075
0,25	0,75	0,908	1,095
0,27	0,73	0,897	1,1
0,3	0,7	0,8879	1,14
0,4	0,6	0,8434	1,17
0,5	0,5	0,7936	1,2
0,6	0,4	0,7364	1,36
0,7	0,3	0,6694	1,48
0,8	0,2	0,5848	1,7
0,9	0,1	0,4642	2,15
0,95	0,05	0,3684	2,73
0,99	0,01	0.216	4,6
0,995	0,005	0,171	5,9
0,999	0,001	0,100	10,0
→1	→0	→0	→∞

1) Ya [Yander].

Obviously, the ratio between the conversion rates as computed by Equations (153) and (154) is expressed by a quantity

$$\left(\frac{dQ}{d\tau}\right) \cdot \left(\frac{dQ}{d\tau}\right)_s = (1-a)^{-\frac{1}{3}}.$$

It will be seen from the data of Table 25 and Fig. 69, which

represent the dependence of the ratio between these rates as a function of the quantity G, that at degrees of conversion of 27, 50 and 95% and higher, the conversion rates computed from Equations (153) and (154) differ from one another by factors of 1.1, 1.2, 2.73 and more, respectively.

It is no less important to establish the difference in the theoretical process duration necessary to reach a given value of G as computed by Equations (151) and (152). The data of Table 26 and Fig. 70 characterize the scales of this difference.

Let us note that the ratio between the values of the necessary conversion time as computed after Yander and by Equation (151) is most easily obtained by dividing Yander's expression $x^2 = K\tau$ by Equation (145) and substituting $\underline{x}$ in the quotient by its value from Expression (150).

We obtain as the result

$$\frac{\tau_{\mathbf{g}}}{\tau} = \frac{1}{1 - \frac{2}{3}\left(1 - \sqrt[3]{1 - G}\right)}.$$

As will be seen from the data of Table 26 and Fig. 70, e.g., for the 90% conversion, the calculation following Yander leads to a value of the necessary process time that is 56% larger than that according to Equation (151). The time necessary for 100% conversion of substance B is 3 times as long according to Yander than according to Equation (151).

The possibility of describing the kinetics of reactions in various powdered mixtures by the approximate equation (151) for the diffusion kinetics of reactions in spherical particles has been checked experimentally and confirmed in the work of many authors (here we can present only some of the data that they obtained).

Thus, Ginstling and Fradkina [231] showed that the experimental

- 280 -

TABLE 26

Ratio τ_{Ya}/τ for Various Values of G

G	$\frac{A'}{A''}$,		$3 \frac{\tau_{Ya}}{\tau}$
	1) according to Equation (151)	2) according to Equation (152)	
0.1	0.00113	0.00115	1.02
0.15	0.00285	0.00275	1.04
0.2	0.0019	0.0052	1.05
0.3	0.0116	0.0128	1.09
0.4	0.0216	0.0242	1.12
0.5	0.0369	0.0428	1.155
0.6	0.0567	0.0604	1.22
0.7	0.0851	0.1104	1.305
0.8	0.1247	0.1724	1.385
0.9	0.1846	0.387	1.56
0.95	0.2333	0.5625	2.15
1.0	0.333	1.0	3.0

1) According to Equation (151); 2) according to Equation (152); 3) τ_{Ya}/τ.
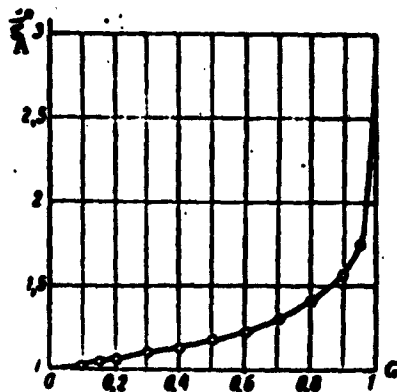
Fig. 70. τ_{Ya}:τ as a function of degree of conversion. A) τ_{Ya}/τ.

data on the reaction kinetics of calcium carbide with molybdenum oxide (Table 27, Fig. 71) and soda with silicon dioxide (Table 28, Figs. 72 and 73) correspond to this equation.

Toropov and other investigators [369] established the same correspondence for the process in which bicalcium silicate forms from calcium carbonate and silica at 1350° and Fadeyeva [370] demonstrated it for the process in which sodium ferrite is produced from soda and ferric oxide at temperatures of 720 and 820°. Luginina [371] demonstrated the possibility of describing the kinetics of silicate formation in the $CaCO_3$-SiO_2-CaF_2 system at a temperature of 1200° by the use of Equation (151).

Averbukh et al. [372] obtained satisfactory agreement between their experimental data and calculations by Equation (151) for the process in which Cr_2O_3 is oxidized in chromite charges at temperatures

TABLE 27

Kinetics of Reaction Between Calcium Carbonate and Molybdenum Oxide* (with $[CaCO_3]:[MoO_3] =$
$= 1$, grain sizes $r_{CaCO_3} = 0.153$ mm, $r_{MoO_3} = 0.036$ mm and $t = 600°$)

τ мин.	G	$10^2 \cdot I$	$10^2 \cdot K$	$10^2 \cdot I_a$	$10^4 \cdot K_a$
3.5	0.0455	0.24	0.68	0.29	0.83
7	0.0909	0.93	1.33	1.07	1.53
10	0.1354	2.1	2.1	2.29	2.29
13	0.1819	3.08	3.06	4.21	3.24
15.5	0.2272	6.38	4.12	6.75	4.35
44	0.5255	41.5	9.45	48.6	11.05
47.5	0.546	45.3	9.55	52.5	11.15
51.5	0.5635	48.93	9.5	58.5	11.3
55	0.581	52.63	9.55	63.4	11.51
60	0.6	57.1	9.55	63.4	11.53
64.5	0.618	61.5	9.55	75.4	11.67
69	0.6355	66.08	9.58	81.65	11.81
74	0.6545	60.57	9.54	89.7	12
80	0.6725	76.67	9.55	96.4	12
86.5	0.691	82.25	9.5	104.88	12.12
95	0.709	88.23	9.5	113.7	12.2
99.5	0.727	94.49	9.5	123.44	12.4
106.5	0.7455	101.4	9.55	134.1	12.6
113.5	0.764	108.77	9.55	145.9	12.76
122	0.782	116.47	9.55	158.6	13
130.5	0.8	124.67	9.55	172.4	13.2
140	0.818	133.55	9.52	185	13.35

* With $G > 0.5$, the process is limited by diffusion.

1) τ, minutes; 2) $10^3 \cdot I_{ya}$; 3) $10^4 \cdot K_{ya}$.

of 900 and 1000°.

Finally, Chishmaru [373, 374], who made a detailed study of reactions in the $CaSO_4$-SiO_2 system at high temperatures, found that Equation (151) expresses the kinetics of these reactions most accurately.

The linear nature of the dependence of I(G) on the time τ of the process was established experimentally in References [231, 369, 371, 373] for a very long time during which the rate of the process is limited by internal diffusion; the same sources also show the inadequacy of Equation (152) for description of the kinetics of diffusion processes in powdered crystalline mixtures. In all of these studies,
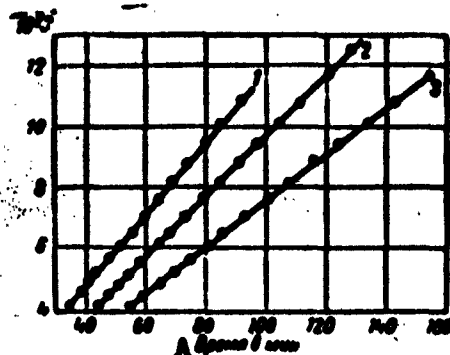
Fig. 71. Kinetics of chemical transformation of equimolar mixture of calcium carbonate with molybdenum oxide with grain size r_{MoO_3} = 0.036 mm and temperatures of 580 and 600°. 1) r_{CaCO_3} = 0.13 mm, t = = 600°; 2) r_{CaCO_3} = 0.153 mm, t = 600°; 3) r_{CaCO_3} = = 0.13 mm, t = 580°. A) Time in minutes.

Equation (152), which was obtained by transforming Yander's Formula (93) in accordance with the theoretical considerations presented above, was found valid only for very small degrees of conversion of the "coated" reagent.

It would, of course, be of interest to describe the diffusion kinetics of reactions in solids using a generalized expression that is valid for particles of any shape. Here, we may proceed from the following considerations [373].

Let a particle of reagent B, which forms a product AB on reacting with reagent A, have the volumes V_1 and V,
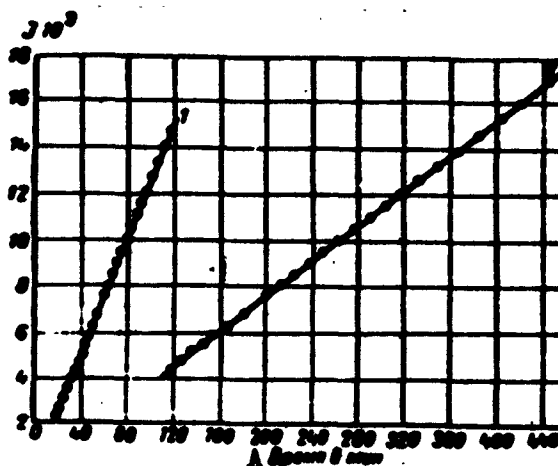
Fig. 72. Kinetics of reaction of soda with silicon dioxide with [SiO_2]: [Na_2CO_3] = 2, reagent grain size r = = 0.036 mm and temperatures of 1) 820°; 2) 800°. A) Time in minutes.

the masses $V_{1\rho}$ and V_ρ and the surface areas F_1 and F at the initial

- 283 -
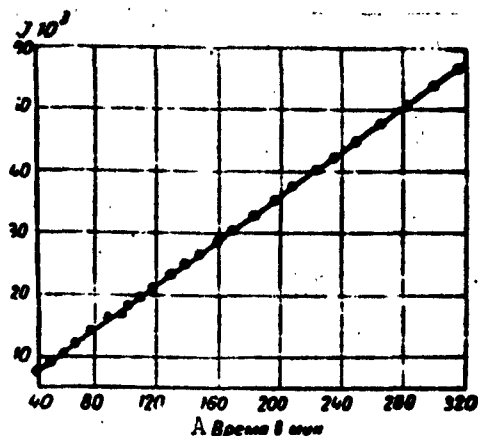
Fig. 73. Kinetics of reaction
of soda with silicon dioxide
with $[SiO_2]:[Na_2CO_3] = 1$, re-
agent grain size $r = 0.036$ mm
and $t = 820°$. A) Time in
minutes.

TABLE 28

Reaction Kinetics of Soda With Silicon Dioxide*
With $[SiO_2]:[Na_2CO_3] = 1$, Reagent Grain Size
$r = 0.036$ mm and $t = 820°$

1 τ мин.	σ_{SiO_2}	$10^n \cdot I$	$10^n \cdot K$	2 $10^n \cdot I_a$	3 $10^n \cdot K_a$
41,5	0,2458	7,58	1,83	7,49	1,81
49	0,266	8,96	1,83	9,6	1,96
58	0,2876	10,6	1,83	11,30	1,96
67	0,307	12,23	1,82	13,3	1,96
77	0,328	14,13	1,83	15,4	2
84,5	0,3416	15,46	1,83	16,8	1,99
92	0,355	16,83	1,83	18,5	2,02
99,5	0,3686	18,22	1,83	20,2	2,02
108,5	0,382	19,83	1,82	21,9	2,03
118	0,396	21,5	1,82	23,9	2,02
127	0,409	23,14	1,82	25,9	2,04
137	0,424	25,03	1,82	28,2	2,05
146,5	0,4366	26,73	1,82	30,4	2,07
157	0,450	28,7	1,82	32,7	2,08
168	0,464	30,81	1,83	35,25	2,1
160	0,4776	33	1,83	37,9	2,1
193	0,492	35,3	1,83	40,9	2,12
206	0,505	37,58	1,82	43,65	2,12
220	0,5196	40,2	1,83	47	2,14
233	0,5322	42,56	1,83	49,9	2,14
248	0,546	45,3	1,83	53,6	2,16
263,5	0,560	48,16	1,83	57,3	2,18
260	0,574	51,14	1,83	61,4	2,19
296	0,5876	54,26	1,83	65,3	2,2
312	0,601	57,34	1,83	69,6	2,24
332	0,6156	60,8	1,83	74,4	2,25

* With $G > 0.24$, the process is limited by diffusion.
1) τ, minutes; 2) $10^3 \cdot I_{ya}$; 3) $10^4 \cdot K_{ya}$.

- 284 -

point in time and after the lapse of a certain time from the beginning of the reaction, respectively.

If during a time $d\tau$, the reaction has passed through a thickness dx of the plane of B corresponding to the mass dV_ρ, then

$$dV_\rho = Fdx$$

or

$$\rho(V_1 - V) = \rho \int_0^z Fdx.$$

From this,

$$dV = Fdx$$

and

$$V_1 - V = \int_0^z Fdx.$$

The extent of conversion of reagent B in fractions of unity may be expressed as

$$G = \frac{V_1 - V}{V_1} = \frac{\int_0^z Fdx}{V_1}.$$

(155)

Differentiating Equation (155), we obtain

$$\frac{dG}{d\tau} = \frac{d\left(\frac{V_1 - V}{V_1}\right)}{d\tau} = \frac{F}{V_1} \frac{dx}{d\tau}.$$

Multiplying the right member of this equation by F/F_1, we obtain

$$\frac{dG}{d\tau} = \frac{F_1}{V_1} \frac{F}{F_1} \frac{dx}{d\tau}.$$

(156)

where F_1/V_1 is the initial specific surface area of the particle and F/F_1 is its relative surface area (which depends on the nature and relative thickness of the layer of product AB and varies during the reaction) and both are grain-shape factors, and $dx/d\tau$ expresses the rate of thickening of the product AB.

F/F_1 is a function of the degree of conversion of reagent B:

$$\frac{F}{F_1} = \varphi(G).$$

The explicit form of this function differs for different geometrical shapes.

Thus, for a sphere $\varphi(G) = (1 - G)^{2/3}$ and

$$G = \frac{\frac{4}{3}\pi R^3 - \frac{4}{3}\pi(R-x)^3}{\frac{4}{3}\pi R^3} = 1 - \left(\frac{R-x}{R}\right)^3. \tag{157}$$

For a solid cylinder, $\varphi(G) = (1 - G)^{1/2}$ and so forth.

The ratio F_1/V_1 may also be expressed as follows:

$$\frac{F_1}{V_1} = \frac{1}{\psi l}.$$

where ψ is the shape factor (which is 1/3 for a sphere, 1/6 for a cube, and so forth) and $\underline{l}$ is the least thickness of the grain.

If we designate $dx/d\tau = \alpha$, Equation (156) may be written in the form

$$\frac{dG}{d\tau} = \frac{1}{\psi l}\varphi(G)\alpha = \frac{\alpha}{\psi l}\varphi(G)$$

and, further, introducing the notation $\alpha/\psi\underline{l} = \chi$, we may obtain a generalized expression for the diffusion kinetics of a reaction in a solid mixture:

$$\frac{dG}{d\tau} = \chi\varphi(G), \tag{158}$$

which, depending on the expressions determining the reaction-rate factor χ and the grain shape factor $\varphi(G)$, may assume the form of Equations (153), (153a) and others.

It will be appropriate here to touch upon the problem of the pseudomicrokinetics of reactions in mixtures of solids.

The situation here is that quite often, without a sufficiently clear conception of the reaction mechanism, an experimentally established kinetic law for a reaction leads to an erroneous conclusion as to its limiting stage.

A characteristic example of this phenomenon is the pseudomono-molecular reaction, the kinetic equation of which is governed by a special case of the diffusion kinetics of the process.

As we know, the rate of certain processes pertaining to the diffusion region, i.e., processes that take place with a diffusion layer of constant thickness, can be expressed by the equation of a first-order reaction.

Thus, if a solid substance A reacts with a liquid substance B to produce a solid product AB that forms with reagent B a mixture that melts at the temperature of the process, then the diffusion layer of the product AB grows continuously on the A side and goes over into the liquid phase on the B side.

In this case, the thickness of the product AB diffusion layer may have a practically constant very small value over a considerable period of time.

The reaction product AB, which goes over into the liquid phase, forms a more or less homogeneous mixture (melt, solution) with reagent B, in which the concentration of B falls off continuously as the process advances.

Since the diffusion resistance of the solid product AB is considerably higher than that of the liquid, the concentration of reagent B at the boundary between the layers AB_t and $(A\dot{B} + B)_{zh}$ is practically equal to its concentration in the liquid (AB + B). Thus, this concentration of B at the outer surface of the product layer AB_t also changes continuously as the process advances.

The concentration of B at the AB-A boundary is equal to or close to zero, since the rate of chemical reaction is incommensurately higher than the diffusion rate.

In view of the above, the process rate in the diffusion region

$$\frac{dx}{dt} = \frac{DAC}{x}.$$

can be expressed with a high degree of approximation for this case as

$$\frac{dQ}{dt} = KCF.$$

And since for a stoichiometric mixture of the reagents, the concentration of substance B at the boundary between AB_t and $(AB + B)_{zh}$ is

$$C = K''(1 - Q)$$

and the cross-sectional area of the diffusion flow (or the surface AB_t) is

$$F = K(1 - Q)^{\frac{2}{3}};$$

then the diffusion rate and the rate of the entire process as a whole vary in this case in accordance with the change in concentration of the unreacted substance B in the $(AB + B)_{zh}$ mixture and the cross-sectional area of the diffusion flow after Equation (117).

In the particular case in which F = const over the entire course of the process (reaction between tablets), the variation of its rate takes place following a law corresponding to monomolecular reaction:

$$\frac{dQ}{dt} = K(1 - Q).$$

§6. PROCESSES LIMITED BY ADSORPTION, SUBLIMATION AND OTHER PHENOMENA. CHANGE IN REACTION KINETICS DURING ITS PROGRESS. TRANSITIONAL REGION

Under practical conditions, the kinetics of a process may be defined not only by the rate of the chemical reaction itself (§3), seed formation (§4) or internal diffusion (§5), but also by other phenomena.

When the slowest stage in a chemical reaction taking place in a solid mixture is sintering, recrystallization, adsorption or some other "elementary" process, the laws governing the variation of its rate will naturally determine the kinetics of the entire reaction.

Thus, if it is limited by adsorption (of particles of one reagent

onto the grain surfaces of the other), then

$$\frac{dG}{dt} = KP_A \frac{1}{1 + P_A b_A}.$$ (159)

where P_A is the partial pressure of the adsorbed reagent over the adsorbent and b_A is a constant;

if it is limited by sublimation of one of the reagents, then, according to what was said in §4 of Chapter 2 (see also [231, 346]), the kinetics of the process may be described by Equations (81a) and (83), in which G will express the extent to which the sublimating substance is converted into the product;

if the reaction is limited by sintering, the intensity of the process may depend on the average radius of the "contact circle" between grains, which was defined by Equation (53), and so forth.

It is clear from the above (§§2-5) that the value of the motive forces and resistances in the individual stages of the reaction and, consequently, the relationship between the possible rates of its various stages may change during the reaction process. As a result, a fundamental change in the reaction kinetics may take place as a function of time. It is possible, for example, that in the initial period of the reaction, with a negligibly small diffusion resistance of the product layer, its rate may be limited by the rate of the actual chemical reaction at the phase boundary, and later, after the [product] layer has thickened considerably, by the rate of diffusion of the reagents in it. Here, as in other similar cases, the reaction kinetics during the various stages must be described by different equations, in accordance with the transitions of the process from one region, e.g., from the region of chemical kinetics, into another — e.g., into the diffusion region.

Such transitions of the process from one region into another may

TABLE 29

Kinetics of Reaction Between Calcium Carbonate and Molybdenum Oxide* With $[MoO_3]:[CaCO_3] =$ = 3, grain sizes r_{CaCO_3} = 0.13 mm, r_{MoO_3} = 0.064 mm and t = 580°.

l ; мм.	G**	$10^2.F$	$10^4.K$	$10^2.J$	$10^4.K$
18	0.0757	50.9	2.82	—	—
22	0.909	61.53	2.78	—	—
26	0.1061	72.07	2.75	—	—
30	0.1213	82.6	2.75	—	—
32.5	0.1303	88.9	2.73	—	—
35	0.1392	95.1	2.74	—	—
38.5	0.1485	101.63	2.64	—	—
62.5	0.581	—	—	—	—
66.5	0.6	—	—	57.1	8.6
71.5	0.618	—	—	61.5	8.6
76.5	0.6355	—	—	66.08	8.65
81.5	0.6545	—	—	70.57	8.65
88.5	0.6725	—	—	76.67	8.6
95	0.641	—	—	82.25	8.66
102	0.709	—	—	88.23	8.65
109	0.717	—	—	94.49	8.65
117	0.7455	—	—	101.4	8.65
126	0.764	—	—	108.77	8.63
135	0.782	—	—	116.47	8.64
144.5	0.8	—	—	124.67	8.64
155	0.818	—	—	133.55	8.65
166	0.836	—	—	143.07	8.63
178.5	0.855	—	—	153.95	8.64
192	0.873	—	—	165.3	8.6

* The process is limited first by sublimation and then by diffusion.

** For $\tau < 38.5$, G expresses the extent of conversion of the MoO_3, and subsequently that of $CaCO_3$.

1) τ, minutes.
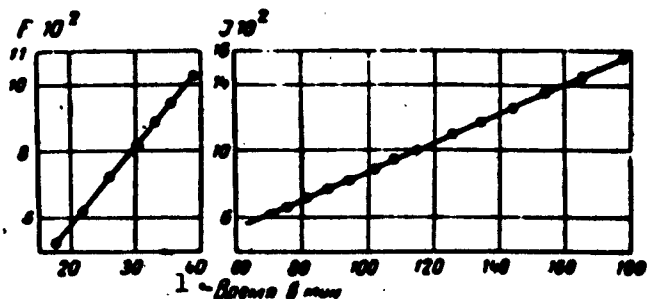
Fig. 74. Kinetics of reaction between calcium carbonate and molybdenum oxide with $[MoO_3]:[CaCO_3]$ = 3; r_{CaCO_3} = 0.13, r_{MoO_3} = 0.064 and t = 580°. 1) Time in minutes.
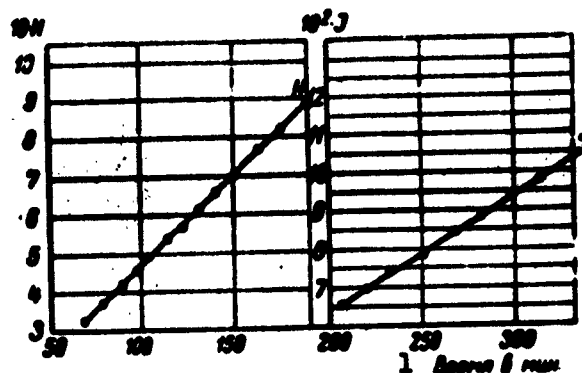
Fig. 75. Kinetics of reaction of soda
with silicon dioxide in the presence
of NaCl with $[SiO_2]:[Na_2CO_3] = 1$; $r =$
$= 0.036$ mm and $t = 750°$. 1) Time in
minutes.

be observed in practice. Thus, Ginstling and Fradkina [231] established
that when molybdenum oxide reacts under certain conditions with cal-
cium carbonate, the rate of the process is limited first by sublima-
tion of the molybdenum oxide and subsequently by its diffusion through
a layer of calcium molybdate that forms as a result of the reaction.
In accordance with this, the process kinetics is expressed first by
Equation (82a) and later by Equation (151) (Table 29 and Fig. 74).

The same authors [231] demonstrated transition of the process
from the region of the actual chemical kinetics into the diffusion
region in the reaction of silicon dioxide (quartz) with soda. Running
this reaction at a temperature of $750°$ in the presence of NaCl, we
may observe a radical change in the reaction kinetics over time
(Table 30, Fig. 75).

Luginina [371] noted such a change for the process in which
calcium silicate is produced from silicon dioxide (quartz) and $CaCO_3$.

The actual transition of the process from one region (e.g., the
reaction at the interface) to another (e.g., diffusion in the bulk of
the phases) may, depending on the conditions of the process, occupy

- 291 -

TABLE 30

Kinetics of Reaction Between Soda and Silicon Dioxide* in the Presence of NaCl With $[SiO_2]$: $[Na_2CO_3] = 1$, $r = 0.036$ mm and $t = 750°$.

τ мин.	a_{SiO_2}	$10 \cdot H$	$10^5 \cdot K$	$10^5 \cdot l$	$10^5 \cdot K$
1,5	0,0341	—	—	—	—
3	0,0683	—	—	—	—
4,5	0,1022	—	—	—	—
67,5	0,3413	3,22	4,76	—	—
78	0,376	3,7	4,75	—	—
89	0,409	4,21	4,74	—	—
96,5	0,430	4,55	4,72	—	—
104	0,450	4,9	4,71	—	—
114,5	0,4775	5,43	4,76	—	—
121,5	0,492	5,7	4,70	—	—
130,5	0,5115	6,15	4,71	—	—
140,5	0,5325	6,63	4,72	—	—
151	0,5525	7,12	4,72	—	—
163	0,574	7,7	4,72	—	—
175	0,594	8,25	4,72	—	—
189	0,6145	8,9	4,71	—	—
206	0,635	—	—	65,37	3,19
219,5	0,649	—	—	69,73	3,17
232	0,662	—	—	73,57	3,16
251	0,6835	—	—	78,43	3,12
268	0,696	—	—	83,9	3,14
282	0,710	—	—	88,57	3,14
298	0,724	—	—	93,43	3,14
313	0,737	—	—	98,17	3,14
330	0,751	—	—	103,53	3,14

* The process is limited first by the reaction and then by diffusion.

1) τ, minutes.

a longer or shorter span of time.

In reactions between crystalline solids, it is frequently necessary to deal with a transitional region in which the rate of the over-all process is limited and determined by the rate of two or more phenomena simultaneously; sometimes a transitional region occupies the entire time span during which observations are conducted. At any rate, it merits the attention of investigators, the more so because study of "mixed" kinetics in the reactions under consideration has thus far not produced simple and exact expressions for many practical cases.*

Using the so-called quasistationary method or the method of the equal-access surface, we may obtain an approximate but quite general

solution to the mixed-kinetics problem [78].

We shall regard the reaction surfaces of the grains to be equally accessible for diffusion and the diffusion conditions as independent of whether or not a reaction takes place on this surface.

Let the reaction rate at the surface, which depends on the concentration of the reacting substance at this surface, be $f(C')$.

In the stationary or quasistationary state, the reaction rate is equal to the quantity of material diffusing toward the reaction surface, and is expressed by the formula

$$f(C') = \beta(C - C'),$$ (160)

where β is the rate constant of diffusion and C is the concentration of the diffusion substance at the external surface of the diffusion layer.

The diffusion rate constant β is analogous to the heat-transfer coefficient and may be determined from the equation of specific diffusion flux:

$$q = \frac{dQ}{F dt} = \beta \Delta C.$$ (161)

Since q has the dimensions of moles/$cm^2 \cdot$ sec (or g/$cm^2 \cdot$ sec), while ΔC is given in moles/cm^3 (or g/cm^3), the dimensions of β are cm/sec.

Solving Equation (160) for any explicit form of $f(C')$, we may obtain C' as a function of C and then the value of the reaction rate in the mixed region.

In the simplest case, in which F = const (tablet reaction) and the reaction at the surface is of the first order

$$f(C') = kC',$$

Equation (160) assumes the form

$$\beta(C - C') = kC',$$ (162)

from which

$$C' = \frac{\beta}{k+\beta} C.$$

(163)

Here, the reaction rate for the quasistationary process is

$$\frac{dG}{dt} = \frac{k\beta}{k+\beta} C.$$

(164)

Since in this case the macroscopic reaction rate also follows the first order, we may write

$$\frac{dG}{dt} = K^{\cdot}C,$$

(165)

where

$$K^{\cdot} = \frac{k\beta}{k+\beta}.$$

(166)

Considering, instead of the rate constants of reaction and diffusion, their reciprocals, we obtain in this simplest case

$$\frac{1}{k^{\cdot}} = \frac{1}{k} + \frac{1}{\beta}.$$

(167)

i.e., the diffusion and chemical resistances to the process simply add.

Obviously, the equation will be greatly simplified if the values of the quantities $\underline{k}$ and β are not comparable, i.e., when the process does not belong essentially to the transitional region.

Thus, with $k \gg \beta$, we find that $K^* \cong \beta$ and the rate of the process is determined by the diffusion rate; in this case, the process rate will naturally be independent of the chemical reaction mechanism. With $k \ll \beta$, we get $K^* \cong k$ and $C' \cong C$ and the rate of the over-all process will depend wholly on the rate of the actual chemical reaction.

Let, as before, the reaction process between A and B (see page 185) consist of sublimation of reagent A, its diffusion toward reagent B, and reaction between them to form a product AB.

Let us adopt the following notation for our analysis of this process:

W_v, W_r and W_d: the resistances to sublimation, reaction and diffusion, respectively; C_0, C_1 and C_2: the respective concentrations of the sublimating reagent at the surface of its own grains, at the outer surface of the product diffusion layer, and at the reaction surface of the second ("coated") reagent; C_B: the concentration of the second reagent at the AB-B interface; F_1, F_2 and F_3: the respective areas of the reaction surface, the smallest cross section of the diffusion flux, and the sublimation surface.

Obviously, the over-all concentration gradient, which expresses the motive force of the process

$$\Delta C = f(C_0, C_1, C_2, C_B) = (C_0 - C_1) + \\ + (C_1 - C_2) + (C_B \cdot C_2) = C_0 - C_2(1 - C_B). \qquad (168)$$

With $C_B = 1$, the motive force of the process is nothing else but the concentration of the sublimating reagent at the surface of its grains: $\Delta C = C_0$ and, under isothermal conditions, is a practically constand quantity.

If the process consists solely of sublimation and reaction or of diffusion and reaction, we have, respectively,

$$\Delta C = C_0$$

and

$$\Delta C = C_1.$$

In all of these cases, ΔC = const, so that Equation (103) may be rewritten in the form

$$\frac{dQ}{dt} = K \frac{1}{\Sigma \frac{W}{F}}. \qquad (169)$$

With $F_1 = K_1 F_2 = \ldots = K_{i-1} F_i = \ldots = K_{n-1} F_n$, i.e., in the case, for example, of a stoichiometric mixture, Equation (103) assumes the form

$$\frac{dQ}{dt} = \frac{F}{K_1 W_v + K_2 W_b + K_3 W_d}. \qquad (170)$$

In its general form, this approximate equation expresses the rate of a process of the type described as a function of the basic factors determining it. Obviously, the problem consists in finding the form of the functions $W_v = f(G)$, $W_r = \varphi(G)$ and $W_d = \psi(G)$, which reflect the laws governing the variation of the principal resistances to processes of this type as they unfold.

Numerous attempts to describe mixed reaction kinetics in crystalline mixtures have become known. For the reasons indicated above, they usually either involve significant simplifications of the problem (first trend) or (second trend) result in complex expressions that are more exact but less easily handled for practical purposes. The work of Fishbek [78] is worthy of mention among the studies of the first trend. His reasoning as to the kinetics of solid-phase reactions in the transitional region may be reduced to the following.

Let two substances react with one another with formation of a diffusion layer of their compound in such a way that the rate of the actual reaction and the rate of diffusion are comparable with one another. This may occur, for example, in cases where the concentration gradient $\Delta C'/x$ of the diffusing agent in the product layer represents a considerable quantity, i.e., with very small values of the thickness x of this layer.

In these cases, the total concentration gradient of the diffusing reagent is

$$\Delta C = \Delta C' + \Delta C'',\tag{171}$$

where $\Delta C'$ is the concentration gradient of this reagent in the product layer and $\Delta C''$ is the same gradient at the boundary between the product and second-reagent phases.

It is obvious that on the one hand

$$\Delta C' \Big|_{} = 0$$
$$\Delta C'' \Big|_{} = \Delta C$$
$$x \Big|_{} = 0,$$

(172)

while on the other

$$\Delta C' \Big|_{} = \Delta C$$
$$\Delta C'' \Big|_{} = 0$$
$$x \Big|_{} = \infty.$$

(173)

In view of the above, we may, in a simple (and quite coarse) approximation, regard $\Delta C''$ as proportional to $\Delta C'/x$, i.e.,

$$\Delta C'' \quad K_1 \frac{\Delta C'}{x}.$$

(174)

On the basis of Equation (171),

$$\Delta C' \quad \Delta C \frac{x}{x + K_1}$$

(175)

and

$$\Delta C'' = \Delta C \frac{K_1}{x + K_1}.$$

(176)

On this basis, regarding the diffusion layers of the product as flat and remembering that

$$\frac{dx}{d\tau} \quad K \frac{\Delta C'}{x}.$$

applies for such layers, Fishbek obtains the equation

$$\frac{dx}{d\tau} = K \Delta C \frac{1}{x + K_1},$$

(177)

which, after separation of variables and integration, assumes the form

$$\frac{x^2}{2} + K_1 x = K' \tau$$

(178)

or

$$x + \frac{x^2}{2K_1} - \frac{K'}{K_1} \tau = K'' \tau,$$

(179)

which differs in form from Yander's Equation (91).

With $x < K_1$, Expression (179) is easily reduced to the form

$$1 + \frac{x}{K_1} + \frac{x^2}{2K_1^2} = \frac{K_1 \tau}{K_1^2} + 1 = e^{\frac{x}{K_1}},$$

from which

$$x = K_1 (\ln K' - \ln K_1^2 + \ln \tau).$$ (180)

If, following Fishbek, we now disregard the quantities $\ln K^1$ and $\ln K_1^2$ as small by comparison with $\ln \tau$, we may easily obtain the expression

$$x = K_1 \ln \tau,$$

or, otherwise expressed

$$\frac{dx}{dt} = \frac{K}{\tau},$$

which is consistent with Tammann's Equation (88).

It therefore follows from the above that Equation (88) may serve for highly approximate description of the kinetics of these processes in the transitional region.

Nevertheless, the validity of Fishbek's reasoning and conclusions is relative. Their inadequacy is due to the author's use of simplified conceptions concerning the mechanism of reactions between solids, his use of the unjustified assumptions noted earlier (specifically, the assumption that the diffusion layers are planar) in his reasoning and derivations, and the nonrigorous solution of certain equations.

It is impossible in the present monograph to delineate the studies that have been made in the second trend, which propose to describe circumstantially and rigorously the kinetics of these reactions in the transitional region. It is sufficient to note that these studies (they include, for example, the investigation of Stal'khane and Mal'mberg [375]) have not yet resulted in the derivation of equations that can be used for direct description of the kinetics of real reactions in crystalline mixtures over any broad range of conditions (attention has been drawn to this by Yesin and Gel'd [368], among others), and essentially represent simply various mathematical formulations of the problem as applied to various particular cases.

Manu-script Page No.	[Footnotes]

239   Equation (94) is considered in detail in §3 of Chapter 7.

250   Crystallization kinetics, a special study of which appears in the well-known works of Fol'mer [347], Bochvar [348], Frenkel' [44, 45], Danilov [162], and certain other authors, is a separate and rather broad field and is not considered here. The reader will find an exposition of the contemporary theory of this process in the second volume of the book by Yesin and Gel'd [368].

256   Equations (96) and (114) naturally also describe the kinetics of reactions whose rate is independent of the concentration of the reagents at the contact surface.

269   The preliminary results of these works were reported at the Conference on Heterogenous Catalysis in May 1940.

273   When C is the molar concentration, $\epsilon = \frac{\mu}{\rho}$. If C is the concentration by weight, $\epsilon = \frac{\mu\mu_1}{\rho_1}$, where μ_1 is the molecular weight of A.

292   Certain premises concerning this were briefly touched upon in §2 of this chapter.

Manu-script Page No.	[List of Transliterated Symbols]

237   з = z = zerno = grain

256   т = t = tverdoye telo = solid

256   ж = zh = zhidkost' = liquid

260   ср = sr = sredniy = average

278   я = ya = Yander

295   в = v = vozgonka = sublimation

295   р = r = reaktsiya = reaction

295   д = d = diffuziya = diffusion

Chapter 6

PRINCIPLES FOR CLASSIFICATION OF
REACTIONS IN CRYSTALLINE MIXTURES

The important and quite complex problem of classifying reactions that take place on heating of crystalline solids has been touched upon in relatively few studies. Yander, Myuller, Khyutting, Yost, Garner, Pozin and Ginstling, Khaufe and certain other investigators have been concerned with it.

While they do not solve this problem completely, the work of these investigators enables us to map out basic principles (or criteria) for classifying reactions in solids that facilitate systematic study and description of these reactions.

The first attempt at systematizing solid-phase reactions was undertaken about 30 years ago by Yander [376]. The basis for the classification that he proposed is the nature of the chemical reaction between the solids. Accordingly, Yander divides reactions between solids into the following groups.

1. Reactions of a basic oxide with an acidic oxide; e.g., some oxide such as BaO, CaO, SrO, MgO, ZnO, PbO, CdO, NiO, FeO, CoO, CuO, etc., with some acidic oxide such as WO_3, MoO_3, SiO_2, TiO_2, V_2O_5, Fe_2O_3, etc., in a reaction of the type

$$BaO + WO_3 \rightarrow BaWO_4.$$

2. Reaction of a salt of carbonic or sulfuric acid with a basic oxide, accompanied by displacement of the acid anhydride toward the oxide; for example, the reaction of strontium, calcium or magnesium

carbonate with oxides of barium, strontium, calcium and the sulfates of Ca, Sr, Mg, Co, Ag, Pb, Cu with oxides of Ba, Sr, Ca, Pb, Mg, etc., according to the type

$$AgSO_4 + PbO \rightarrow PbSO_4 + Ag_2O.$$
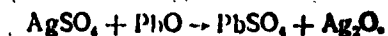
3. Substitution of the CO_2 in a carbonate by a solid acidic oxide; for example, the reaction between $CaCO_3$, $SrCO_3$, $BaCO_3$ and SiO_2, MoO_3, WO_3, according to the type

$$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2.$$

4. Substitution of the metal in salts, oxides or sulfides by another metal, which takes place, for example, on heating of magnesium with oxides of zinc, tellurium, cadmium, copper, or nickel; on heating of Zn with CuO, PbO, or AgI; of Fe with PbO, CuO; Pb with CuO, and so forth, for example

$$Mg + ZnO \rightarrow MgO + Zn.$$
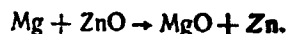
5. Exchange decomposition on reaction of a carbonate with a sulfate, according to the type

$$BaSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + BaCO_3.$$
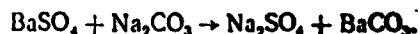
This reaction grouping of Yander, which was unquestionably useful to investigators in its time, is now of historical rather than theoretical and applied importance.

Indeed, it is not difficult to perceive that reactions of group 2, in which part of component A is separated from it and combines with component B, are similar to reactions of group 4, in which the same phenomenon occurs. From the standpoint of systematization of the chemical reactions, the difference that exists in this case between the chemical compositions of the part split off from A and the part that moves toward B is nonessential, because its composition does not determine the fundamental nature of the relationships governing the process. A large number of technically important reactions between

- 300 -

solids, such as, for example, reactions in which metal sulfates are reduced by carbon, the reactions between phosphates and metallic oxides, and others, do not fit into Yander's classification.

At the present time, when solid-phase processes are numbered in the thousands, such a classification, which takes note only of certain general features (chiefly concerned with the chemical composition of the initial components), is of limited value.

An attempt to classify chemical reactions from a technical standpoint was undertaken at one time by Myuller [377]. Taking into account the fact that, in general, it is possible for a solid to react with a solid, a liquid or a gas, for a liquid to react with a liquid or a gas, for a gas to react with a gas and for a solid to react simultaneously with a liquid and a gas, Myuller accordingly classifies all chemical reactions into seven classes. Further, assuming that the reaction of each pair of bodies (e.g., solid with solid) can give seven different (as regards the combination of physical states) products, he distinguishes seven types of reaction in each class.

Thus, class 1 of Myuller's system (solid + solid) encompasses the types:

1) $T + T \rightarrow T + T$;
2) $T + T \rightarrow T + Ж$;
3) $T + T \rightarrow T + Г$;
4) $T + T \rightarrow Ж + Ж$;
5) $T + T \rightarrow Ж + Г$;
6) $T + T \rightarrow Г + Г$;
7) $T + T \rightarrow T + Ж + Г$.

$T = t =$ solid
$Ж = zh =$ liquid
$Г = g =$ gas

As a result, the total number of types over all classes is 49.

Having for the most part practical objectives in mind for his classification, Myuller admitted a number of simplified conceptions of chemical processes in it. Thus, for example, he does not draw a distinction between the concepts of "solid" (one) and "solid + solid"

- 301 -

(two) or, accordingly, between the processes:

a) solid → solid + gas and

b) solid + solid → solid + gas

As a result of this, for example, the reaction in which calcium carbonate dissociates and the reaction in which it interacts with kaolinite to form silicates and other calcium compounds with evolution of CO_2, which have very little in common, fall into the same type.

Furthermore, in assigning a reaction to one type or another, Myuller uses as his guide only the initial and final physical states of the system components, but does not always follow this rule rigorously.

As a result, for example, he classifies the reaction

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$
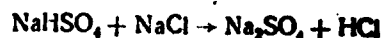
among those of the type $T + T \rightarrow T + G$, while $NaHSO_4$ is in the liquid state at the temperatures at which it reacts with NaCl.

For the same reason, the reaction

$$CuO + C \rightarrow Cu + CO$$
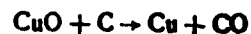
is regarded in this classification as proceeding by reaction of solid with solid, while its progress preferentially through the gaseous phase is much more probable in this case; the scheme here would be

$$CO + CuO \rightarrow Cu + CO_2$$
$$\underline{CO_2 + C \rightleftarrows 2CO}$$
$$CuO + C \rightarrow Cu + CO.$$
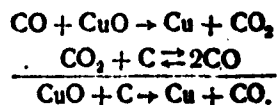
It is precisely in this way that contemporary metallurgy [280, 283, 284, 378-380] treats the mechanism of processes in which metal oxides are reduced by solid carbon.

Nor may we exclude in this case the possibility of dissociation of copper oxide with subsequent binding of oxygen by the carbon.

Further, as a result of his simplified characterization of the processes on the basis of the above criteria, Myuller incorrectly

classifies the Leblanc process, in accordance with its over-all equation

$$Na_2SO_4 + 4C + CaCO_3 \rightarrow Na_2CO_3 + CaS + 4CO;$$

which does not reflect the actual path taken by the interaction of the reagents and intermediate products, among reactions of the type:

solid + solid → solid + liquid + gas, and so forth.

Naturally, such a classification may be of service in certain problems of a practical nature, but it is not capable of assisting in a generalizing investigation of solid-phase processes.

Yost [218] breaks up reactions between solids into the following classes.

A. Reaction between two elements (for practical purposes, according to Yost, we can speak in this case only of metals) with formation of a compound of them, according to the type

$$M' + M'' \rightarrow M'M'' \quad \text{or} \quad mM' + nM'' \rightarrow M'_m M''_n.$$

B. Reaction between two compounds having one component (element, ion or complex) in common, e.g.,

$$mM'X' + nM'X'' \rightarrow (M'X')_m (M'X'')_n$$

or

$$mM'X' + nM''X' \rightarrow (M'X')_m (M''X')_n.$$

C. Reaction between two compounds that do not have a common component, such as

$$M'X' + M''X'' \rightarrow M'X'' + M''X'.$$
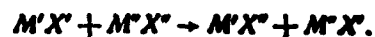
Then Yost divides each class into groups (subclasses) in accordance with the possibility of formation of solid solutions in the system and their nature, e.g.:

1) the initial substances and products (i.e., all components of the system) form solid solutions with unlimited solubility, i.e., are miscible with one another in all proportions;

2) the initial substances and the products form solid solutions

with limited solubility;

3) some of the system components, e.g., the initial substances, do not form solid solutions;

4) neither the initial substances nor the final products form solid solutions.

Further, the reaction types are distinguished from one another in accordance with this classification on the basis of the mobility difference (difference between diffusion rates) between the elements (complexes) of the type M', M" and the type X', X".

Thus, we obtain the following pattern.

A. Reactions of M' with M".

1. a) M' and M" form solid solutions with unlimited solubility. In this case, we have a diffusion process.

b) If M' and M" form solid solutions, but the rate of diffusion of one component into the other, e.g., M" into M', is extremely low, then the final products will be a solid solution (M', M") and the practically pure initial component M'.

2. M' and M" form only solid solutions with limited solubility. In this case, there will be two solid solutions formed in the final reaction product.

3. The two components form an ordered solid phase $M'_m M"_n$ without mutual solution. In this case, the reaction continues until one of the initial components has disappeared. These reaction types are particularly common in metallic systems.

B. Reactions of M'X' with M"X' (and also between M'X' and M'X"). The same reaction types as in case A are also possible in this case. Table 31 shows the simplest types of reactions classified here. An X must be assigned to each M, but the symbol has been dropped here to abbreviate the notation. Reactions of the type M'X' with M'X" proceed

in exactly the same way.

C. Reactions of M'X' with M"X".

1. All components (M'X'; M"X"; M'X"; M"X') form solid solutions with unlimited solubility; here we may distinguish two cases or kinds of these processes:

a) the mobilities of the anions and cations do not differ greatly;

b) the mobilities of the anions and cations differ greatly. Here, the anions most frequently have mobilities lower than those of the cations. In this case, an X'-phase and an X"-phase between which the M' and M" are distributed are observed to form.

2. M'X' and M"X" do not form solid solutions, as was the case with M'X' versus M"X' and M'X" versus M"X". In this case, the reaction is similar to that described above (B).

3. M'X' and M"X" do not form solid solutions and only one of the reaction products forms a solid solution with one of the initial substances, for example, M"X' with M'X'. The process is further distinguished by unlike mobilities of the various particles.

In cases where M' and M" are more mobile (which is most frequently the case), we have only minor distribution of M' and M" at first on the boundary between the two phases; then M" diffuses into M'X' with formation of a solid solution (M'M") X'. A thin layer of M'X" forms between this solid solution and the compound M"X'. When solution of M" is complete, the reaction stops. The reaction's progress is represented in Table 31.

4. M'X' and M"X" and the reaction products form no solid solutions. Here, either of two cases may occur:

a) M' and M" are more mobile. In this case, the M' and M" are distributed on the interface surfaces, with a layer of M"X' forming on M'X' and a layer of M'X" forming on M"X". Thus, we obtain layers of

- 305 -

M'X', M"X', M'X" and M"X":

    b) X' and X" are more mobile. In this case, as described under item a), layers of M'X', M'X", M"X' and M"X" form.

    The process path in which both M and X possess significant mobilities, which is rarely encountered in practice, is considerably more complex. The course of the processes listed is represented schematically in Table 31.

* TABLE 31

Simple Cases of Interaction Between M' and M" (qualitative representation)

1) M' and M" form a solid solution with unlimited solubility; a) rates of diffusion into M' and M" closely similar; b) rate of diffusion of M" into M' very low; 2) M' and M" form solid solutions with limited solubility; 3) M' and M" do not form a solid solution but yield a compound $M'_m M''_n$. A) At start of reaction;

B) concentration distribution during reaction; C) final state; D) concentration; E) solid solution (M', M") of variable composition; F) homogeneous solid solution (M', M"); G) nearly pure M' + solid solution (M', M"); H) same as I; I) solid solution of I and II; J) solid solution (M', M") I and solid solution (M', M") II (quantity of one phase may be = 0; K) three phases: M', M" and $M'_m M''_n$; L) pure component M' + compound.

5. Depending on how case B proceeds from case A, we may accordingly indicate the scheme for cases C in a more general form, going over from $M'X' + M''X'' = M''X' + M'X''$ to the scheme $M'X'O + M''X''O = M''X'O + M'X''O$, and so forth.

Yost correctly regards it as necessary to take the diagram of state of a system into account in assigning it to a given class.

However, as we consider the classification tables of Yost [218], one of which is shown here, we may note the following circumstances:

1) a considerable part of his classification is devoted to processes in which solid solutions form and is not concerned with the chemical reactions;

2) the difference between the mobilities of M', M'' and X', X'', which Yost takes into account, has no essential effect on the nature of the process and the phenomena composing it.

The field of application of this classification is limited chiefly to metallurgical processes. Generalization and more or less detailed subdivision of many other "solid-phase" processes on the basis of this classification is impossible.

Roginskiy [381], who studied topochemical reactions, proposed that they be classified after the following scheme.

I. Reactions in which a crystalline solid decomposes into gaseous products.

II. Reactions in which crystals form from a homogeneous (gaseous or liquid) phase.

III. Topochemical reactions in the narrow sense of the word, which are characterized by the presence of solids in both the initial components and in the reaction products.

In this scheme, the actual "solid-phase" reactions comprise those of class III, but reactions of classes I and II may be component parts

in class III processes. As Roginskiy points out, reactions of class III are widely diversified as regards their chemical nature. They incorporate a broad range of processes, extending from allotropic transformations and decay or formation of compounds of the crystal-hydrate or ammoniate types (for which there is no reason to expect the presence of a chemical heat of activation) to reactions of the type in which oxides and sulfides are reduced and salts with complex anions decompose, i.e., to reactions accompanied by profound chemical transformations (for which we might expect the presence of a rather large true heat of activation).

A characteristic property of this class of reactions is the co-existence of at least two solid phases.

The important classification principle delineated by Roginskiy has been used more than once by other, later investigators.

Expanding Roginskiy's classification somewhat and supplementing it, Garner [23, 262] classifies reactions taking place with participation of solids in the following manner:

1) reactions that do not involve reconstruction of a crystal lattice, i.e., that take place without changes in the solid phase, including

a) reactions in which the product yielded forms a solid solution with an initial reagent and

b) reactions of chemosorption at the surface of the solid;

2) reactions that incorporate a single crystallization step; these include reactions of gases with formation of solids and formation of solids by reactions in solutions;

3) reactions in which destruction of a crystal lattice takes place, e.g., the processes in which mercuric oxide, potassium azide, and the like decompose, in which the solid phase vanishes completely,

- 308 -

yielding gaseous products;

4) reactions in which both destruction and formation of a crystal lattice take place; these reactions, which make up an extremely extensive class, include, as noted by Garner, the following types:

a) $A_t \rightarrow B_t + gas$,

e.g., the decomposition of photographic emulsion on exposure to light;

b) $A_t \rightarrow B_t + C_t$,

e.g., decomposition of silver acetelide, and

c) $A_t + B_t \rightarrow C_t$,
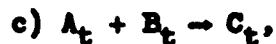
e.g., the formation of spinel from an oxide mixture.

Type "4c" apparently implies a broad range of intersolid reactions that are greatly diversified as regards nature and mechanism. At the same time, a detailed classification of precisely these reactions would naturally be of great interest.

On the whole, this list stakes out a rational classification principle, but it fails to incorporate a number of transformations that take place in the region under consideration, such as $A_t + B_g \rightarrow \rightarrow AB_g$, $A_t + B_{zh} \rightarrow AB_t$, and others.

According to Khyutting [382], who published, in 1941, a generalizing classification for chemical reactions, devoting considerable space to transformations that take place with participation of solids, these reactions are covered by five classes, each of which is divided into a large number of subclasses, which, in turn, unify an exceedingly large number of species and varieties (subspecies) of reactions.

The number of reaction species (which are further classified into subspecies) in certain subclasses of Khyutting's classification is greater than 100. This last circumstance makes it difficult to set forth his classification in any detail and obliges us to restrict

ourselves to a brief characterization of some of its features.

Khyutting selected the number of "component parts" in the reaction system as the basic starting criterion for classifying a process in a given class.

Thus, the soda-production process, which is expressed by the over-all reaction

$$Na_2SO_4 + 4C + CaCO_3 \rightarrow Na_2CO_3 + CaS + 4CO,$$

is classified by Khyutting in class V of his systematization because he discerns in this process five component parts:

$$I = Na, \ II = S, \ III = O, \ IV = C \ \text{и} \ V = Ca.$$

Khyutting assigns this process to the species represented by the scheme

$$ABC_\tau + D_\tau + EDC_\tau \rightarrow ADC_\tau + EB_\tau + DC_{\tau}.$$
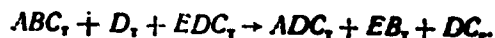
In actuality, the equation given above expresses only the over-all result of a number of reactions that actually take place in the process under consideration, so that it is difficult to assign it to a given class on the basis of this equation. Actually, we have other reactions here that should be classified.

Similar considerations arise in connection with assignment of the majority of other processes to classes III, IV and V.

As concerns the reaction species (of reactions in which solids participate) Khyutting's classification, which recognizes several hundred of them, distinguishes them from one another by the physical state of the initial components and the final reaction products.

For example, subspecies are characterized by different physical states of the intermediate reaction products.

It should be noted that according to the classification principle adopted by Khyutting, processes that have only the same number of "component parts" in their over-all equations in common are assigned

to the same class. This is what restricts the author in subsequent classification. Thus, subclass B_{III} (substitution reactions) of class III in his classification encompasses 89 different reaction species, such as the following:

$$1. \; AB_t + C_r \to AC_r + B_t$$

(example : $CuSO_4 + BaO \to BaSO_4 + CuO$).

$$3. \; AB_t + C_t \to AC_t + B_x$$

(example : $2SO_3 \cdot 3HgO \cdot 2H_2O + HgJ_2 \to 2SO_3 \cdot 3HgO \cdot HgJ_2 + 2H_2O$).

$$13. \; AB_t + C_r \to AC_t + B_t$$

($FeO + C \to CO + Fe$).

$$38. \; AB_x + C_r \to AC_t + B_r$$

($H_2SO_4 + 2K \to K_2SO_4 + H_2$ in the absence of water).

$$43. \; AB_t + C_r \to AC_t + B_r$$

($3Fe_2O_3 + H_2 \to H_2O_{nap} + 2Fe_3O_4$).

$$51. \; AB_x + C_r \to AC_x + B_x$$

($PbS_{почвеннос.} + Fe \to FeS + Pb$).

$$52. \; AB_x + C_x \to AC_x + B_r$$

$$71. \; AB_x + C_r \to AC_x + B_r$$

($CaJ_{2почвенн.} + Cl \to CaClJ + J$).
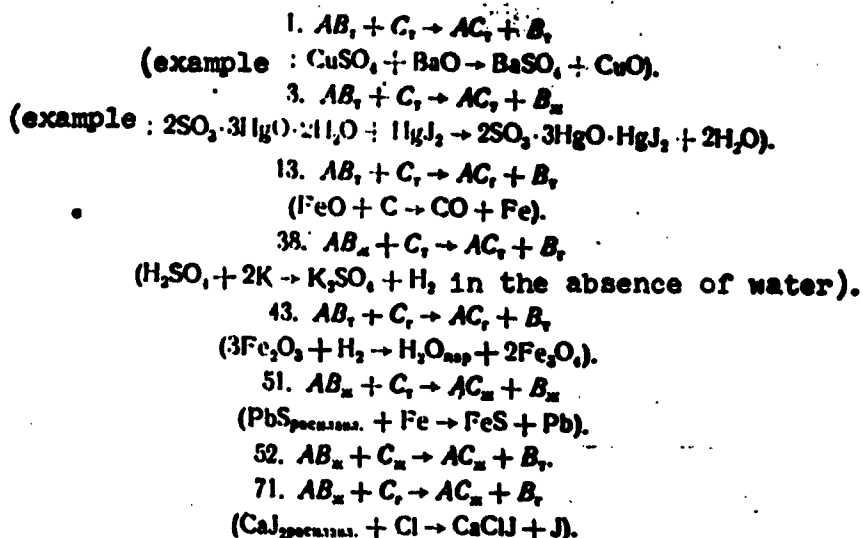
Thus, this subclass combines reactions that take place by completely different routes (e.g., reactions 1 and 52, 3 and 71, and so forth) and, as is easily imagined, are subject to different kinetic laws.

Together with this, we may find reactions that are closely similar in nature assigned to different classes of this system, e.g., in classes II, III and IV.

We are indebted to Khyutting for a highly detailed list and a broad generalization of all conceivable reaction varieties. However, the above peculiarities of his classification limit the possibility of applying it.

We have now set forth the basic studies toward classification of reactions that take place with participation of solids. It is readily observed that these classifications differ greatly from one another. This difference is due primarily to the different objectives that the

various authors had in mind in their work.

Thus, Myuller, pursuing technological objectives, considered that processes of a given type should have approximately the same technological-apparatus formulation. Garner took it upon himself to develop the fundamental ideas of Roginskiy in application to solid-phase processes, but did not go into a detailed classification thereof. Yander's objective was to group solid-phase reactions in accordance with similarities in chemical mechanism. Yost felt it necessary to devote his basic attention to the presence and nature of solid solutions in solid-phase systems. And, finally, Khyutting attempted to give an exhaustive list of all possible reaction varieties, taking into account primarily the number of "component parts" in the reaction mixture, then the physical state of the substances, and so forth.

Each of the studies described above solves only certain particular problems connected with classification of reactions in solid mixtures. As a result, it will also be advisable to devote brief consideration to certain other classification principles for these reactions.

Thus, employing the conventional system of general chemistry, we may classify reactions in solids primarily on the basis of the chemical elements that form the crystalline reagents and products. Here, it is obvious that the reactions of which we are speaking will be broken up into groups in accordance with the formation of compounds of alkali and alkaline-earth metals, copper, zinc, cadmium, lead, tin, iron, aluminum cobalt, nickel, titanium and other metals. The reactions of the oxides of the corresponding metals with other substances will occupy a prime position here.

We may also distinguish between reactions in which such compounds as oxides (metal + oxygen), sulfides and sulfates (metal + sulfur),

silicates (metal + silicon), and so forth, form and react with other substances.

Approximately the same system is used in the work of Budnikov and Berezhnoy [1], and, to some extent, in the present monograph.

This system may be supplemented by a classification of reactions in solids on the basis of other criteria.

Thus, Khauffe [260] classifies the reactions considered in his monograph in the following manner:

$$A_\tau + B_\tau \to C_\tau;$$
$$A_x + B_\tau \to C_\tau;$$
$$A_\tau + B_\tau \to C_\tau;$$
$$A_\tau + B_\tau \to C_\tau + D_\tau;$$
$$A_\tau + B_\tau \to C_\tau + D_\tau;$$
$$A_\tau + B_\tau \to C_\tau + D_\tau;$$
$$A_\tau \to C_\tau + D_r$$
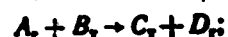
τ = solid
x = liquid
r = gas

It should be noted that the agreement between the numbers of reaction types of interest to us in the classifications of Khauffe and Myuller is accidental: only certain types of Khauffe's classification and class I of Myuller's classification are identical.

Use of modern physicochemical conceptions as to heterogeneous processes would be most useful in classification of reactions in solid mixtures.

As we know, contemporary theory of heterogeneous chemical processes tends to classify and generalize them on the basis of criteria that determine the basic laws governing their progress.

From this standpoint, the most important thing is to find criteria for such physicochemical similarity or dissimilarity between specific "solid-phase" processes that would then enable us to give a more or less exact description of their mechanism and kinetics in terms of certain correspondingly general [similar] or dissimilar expressions.

The reasoning set forth above (pages 188-193) may serve as a basis for such a generalization and differentiation of the reactions studied.

It would appear expedient to classify the processes that take place on heating of mixtures of crystalline reagents into the following prime groups [234]:

1) processes in which particles of the solid react directly with one another;

2) processes that take place with participation of a gaseous phase;

3) processes that take place with participation of liquid phases;

4) processes that take place with simultaneous participation of gaseous and liquid phases.

Table 17 and the diagrams presented above (pages 194-196) may be employed for subsequent classification of reactions that take place on heating of mixed crystalline solids. Actually, it is easy to conceive of a fundamental difference, for example, between the following two reaction types that occur in solid mixtures and are represented by these tables:

IV — reaction with the participation of a gaseous phase that arises as a result of dissociation of one of the reagents (page 197) and

XII — reaction with participation of a liquid phase that arises as a result of melting of one of the reagents in a mixture with an inert material (page 202).

In the former case, the process may be subject to the laws governing dissociation, and in the second it may depend on the type of fusibility curve and the laws governing fusion of the reagent-and-inert-material system.

Let us turn our attention to the classification principles based on the criteria that determine the kinetics of these reactions [383]. As was shown earlier, the kinetics of such reactions may be expressed by one or another relatively simple or complex equation that takes into account the part taken by all phenomena ("elementary processes") that determine the rate of the process.

A very large number of combinations of these phenomena is theoretically conceivable. However, the overwhelming majority of real processes that take place on heating of crystalline mixtures and present practical interest may be examined without incurring any essential error as relatively simple processes that are subject accordingly to the laws governing the progress of some single simple phenomenon that limits the process or two such phenomena.

The latter may serve as a basis for description and classification of the processes under consideration on the basis of this criterion, since its main task should be to generalize and classify reactions that are of practical importance. On this basis, we may map out the four most important large classes of reactions taking place in mixtures of solids:

I) those limited by the rate of the chemical reaction itself;

II) those limited by the diffusion rate;

III) those limited by the rate of chemical reaction and diffusion simultaneously;

IV) those limited by the rate of vaporization or sublimation.

Many processes in which the part taken by physical phenomena is insignificant because of the low rate of the actual chemical reaction, insignificant thickness of the diffusion layer, high diffusion-coefficient values, and other similar causes belong to class I of this list.

Any of the following five phenomena, which define, respectively, five subclasses among processes of this class are possible among the reactions of class I:

1) first-order reaction;

2) second-order reaction;

3) reaction of the reagents at constant concentration, as well as zeroth-order reaction;

4) autocatalytic reaction;

5) several successive reactions.

Subclass 1 of this class includes, for example, the dissociation reactions that are major factors in many processes that take place on heating of crystalline reagents.

Subclass 2 includes, in addition to many other processes, reactions between certain oxides that are of importance in silicate technology.

Subclass 3 includes reactions between two solids and between a solid and a liquid with the latter at constant concentration (as governed, for example, by the composition of the system that melts at the process temperature), and so forth.

Class II encompasses the majority of the so-called solid-phase processes, which involve the emergence of a rather significant diffusion layer of reaction product on the grains of a reagent. If, in the latter case, the rates of the reaction proper and of diffusion are comparable (sufficiently close to one another), the process belongs to class III.

Class IV unifies certain processes in which spinels, sulfides and other compounds form and which are limited by vaporization or sublimation of some substance. Many processes in which a basic oxide reacts with an acid oxide — those studied by Yander [219-222] — would

apparently belong to this class, among others.

Thus, proceeding from the principle described, we may classify all solid reactions that have practical significance.

Here, it is necessary to remember that in accordance with the above, a given chemical transformation in a mixture of solid sub-stances may be assigned to different classes of the above system at different stages of its progress, depending on the relation between the values of the various resistances to the process. Obviously, for example, certain processes accompanied by the emergence of a diffusion product layer and belonging to class I or IV in their initial stage become class II or III processes when the diffusion resistance attains a certain value.

This gives rise to certain difficulties when the classification principle set forth here is applied; this is what constitutes its shortcoming.

Naturally, certain difficulties may also arise in generalization and differentiation of reactions on the basis of the criteria deter-mining their mechanisms: it is much easier to indicate the number of "component parts" or the chemical nature of the materials participat-ing in a reaction than to characterize its mechanism or kinetics.

However, use of either of the last two criteria obliges the in-vestigator to pay careful attention to the essential nature of the re-action in which he is interested and the laws governing it before as-signing it to a given class, or makes it possible, knowing the class of the reaction, to form a judgment as to its mechanism and kinetics and formulate the qualitative laws controlling this reaction. The latter facilitates further study of the reaction and the factors that influence its rate and the composition of its products. Here lies the basic importance of reaction classification on the basis of the cri-

teria that determine their mechanism and kinetics.

Manu-
script   [List of Transliterated Symbols]
Page
No.

311   пар = par = par = vapor

311   расплавл = rasplavl = rasplavlennyy = fused

·Chapter 7

INFLUENCE OF BASIC CONDITIONS OF PROCESS FLOW ON ITS RATE

§1. GRANULOMETRIC COMPOSITION OF MIXTURE

The problem of the most efficient granulometric composition of
the initial charge, or, in other words, the necessary uniformity (or
nonuniformity) and the extent to which its components must be ground,
is one of the most ancient problems of the theory of solid-state reac-
tions and the technology of producing structural, refractory and cer-
tain other materials. In addition to this, it is a pressing problem
and will remain so for a long time to come, since the methods and
correctness of its solution determine the rate, economy and results of
many industrial processes [49, 293, 296, 384-386 and others].

Examination of this problem is particularly appropriate at just
this moment in connection with the broad prospects that are being
opened by the development of new, highly efficient methods for grind-
ing materials (vibration milling, etc.).·

Without pretending that it will represent an exhaustive illumina-
tion of this problem, the authors set out here to treat only certain
aspects of it.

A rather large list of studies has been devoted to the granulo-
metric composition of crystalline solids in connection with processes
that take place when mixtures of them are heated. These papers examine
to one degree of thoroughness or another the influence of grain com-
position in the initial components on the rate of the process in
which they undergo chemical transformation [1, 231, 346, 384 and many

others] and the influence of the heat-exchange process with the surrounding medium [28, 387-390] on properties such as the porosity of products of roasting [49, 296] and the like.

The uniformity and fineness with which the crystalline reagents are found influence the following parameters of "solid-phase" and other processes: •

1) the surface area and surface energy of the granules;

2) the temperature, heat of fusion, and heat of solution;

3) the intensity of heat exchange with the surrounding medium;

4) the rate of solution, sublimation, dissociation and chemical reaction with the other reagents;

5) the thickness of the product layer that forms on the granules during the chemical reaction and the rate of diffusion through it, which is governed by this thickness;

6) the properties of the crystalline reaction properties — physicomechanical, thermal, electrical and others;

7) the behavior (effectiveness) of reaction accelerators for intersolid reactions;

8) the economics of the process.

The above list is sufficient to give an impression of the importance of judgment in selecting the granulometric composition of solid mixtures for conversion processes to be carried out under practical conditions.*

Obviously, the kinetics of reactions in solids are determined primarily by the first, fourth and fifth of the parameters listed above.

It is a generally known fact that, all other conditions the same, the rate of a heterogeneous reaction between substances is proportional to the area of the contact surface between the reacting phases.

In the case of reaction in a mixture of crystalline reagents, this area is not necessarily identical to the area of direct contact between their granules. As was shown earlier (§4 of Chapter 1), the latter is measured in millionths or, more often, in ten-millionths of their total surface and accordingly represents a negligible quantity. When the process of a reaction between granules of crystalline reagents takes place in the presence of a liquid or gaseous phase — a situation that we come up against repeatedly under industrial conditions (pages 188-208), the reaction-surface area at the beginning of the reaction is equal to or nearly equal to the total grain-surface area of one of the reagents and, subsequently, maintains a size of the same order at degrees of conversion markedly lower than 100%. To accelerate such a process, it is, of course, advisable to break up the total grain surface of the appropriate reagent by reducing grain size.

In many cases, reducing grain size also results in an increase in the process rate as a result of a change in the thickness of the reaction-product diffusion layer.

But what, in general, is the link between the rate or degree of a physical, physicochemical, or chemical transformation of a solid mixture and the size of its grains?

The nature of this connection depends on the kind, mechanism and kinetics of the conversion process. This link may naturally be different for processes of recrystallization, sintering, sublimation, fusing and chemical transformation.

It was shown above that the kinetics of reactions in mixtures of solids is rather complex and multi-faceted. It is determined in each specific case by the laws governing the rate variation of the limiting stage of the process and depends on the mechanism and conditions of the reaction's progress. In principle, stages whose rate limits the

over-all process rate may be sublimation, the chemical reaction proper, external and internal diffusion, and others. Since the relationship between the values of the resistances to its various stages may change as the process advances, fundamental changes in its kinetics over time are possible (page 288).

In the overwhelming majority of practical cases, the rates of reactions in solid mixtures are limited by the rate of internal diffusion of at least one of the reagents toward the reaction zone through a layer of product formed on the grains of some reagent, i.e., the kinetics of the process is diffusional.

Here, for mixtures in which the component "coated" by product is monodisperse or nearly so, the kinetics of the process may be described by Equation [151], in which R is the initial grain radius of the "coated" component and τ is time.

With small values of the fraction G of the "coated" component that has reacted, Equation (151) assumes the form

$$\frac{1}{9}G^2 \simeq \frac{K}{R^2}\tau \qquad (181)$$

or

$$G^2 \simeq \frac{k'}{R^2}\tau. \qquad (181a)$$

When G < 0.1, the difference between the results of calculations by Equations (151) and (181a) does not exceed 5%.

Thus, the function I(G) of degree of conversion of the "coated" reagent into the product is inversely proportional to the square of the grain radius of this reagent. However, the dependence of its degree of conversion G on the grain size is more complex.

At the beginning of the diffusion region, when G < 0.2, the degree of conversion of the granules may be assumed in approximation inversely proportional to their radius. Using a diagram of degree of con-
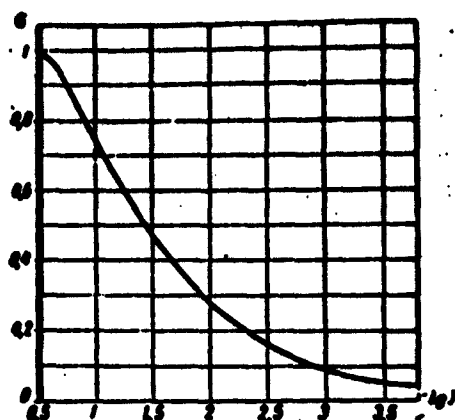
Fig. 76. Logarithm of I as a function of G.

version G vs. the logarithm of T with the negative sign (Fig. 76) [391], we may easily compute that, when the degree of conversion of grains of radius R = 1 is 20%, grains of radii 2, 3 and 4 are converted into the product to 10, 6.8 and 5.2%, respectively, i.e., to degrees smaller by factors of 2, approximately 3 and 4. As the process develops further, the situation

changes and, for example, at the point in time when the degree of conversion of grains of radius R = 1 reaches 100%, grains of radii 2, 3 and 4 have been converted ~70, 50 and 40% into product, respectively. It should be noted that at such relatively high degrees of conversion, the thickness of the product diffusion layer makes up a relatively small fraction of the grain radius of the "coated" reagent, and from this standpoint the indicated conversion-percentage values are relatively small. Let us use Expression (150) to calculate the proportions that apply here. Using this expression, it is easy to find the following values of x/R for various values of G:

G в долях единицы	0,1	0,2	0,3	0,4	0,5	0,6
x в % от R	4	7,5	11,5	16	20,8	26,5

G в долях единицы . . .	0,7	0,8	0,875	0,9	0,95	0,98	1
x в % от R	33,2	42,6	50	53,6	63,2	73	100

1) G in fractions of unity; 2) x in % of R.

Obviously, when 20-30% of the "coated" reagent has been con-

verted, the thickness of the product layer on its grains will amount
to only ~7-10% of their radius. It reaches 0.5R when the reaction has
gone almost to 88%.

These data, which correspond to the law of distribution of matter
in spherical bodies (of which Strelkov [392] wrote in his time), en-
able us to compare the values of x in the examples given above. Thus,
when the thickness of product layer on a grain of unit radius reaches
100%R, it is only about 20%R on a grain having a radius three times
larger.

This circumstance must be taken into account in comparing probable
results of a process not only in different reaction mixtures (mixtures
with the components ground fine to different degrees), but also in
different fractions of a given mixture.

Indeed, in grinding raw material in industry, e.g., in grinding
cement to screen residues of 0.2 to 0.5% on a screen with 900 holes
per 1 cm^2 (No. 200) and from 5 to 8% on a screen with 4900 holes per
1 cm^2 (No. 90), the raw mixture contains grains with sizes ranging
from 1 to 200 μ. Here, approximately 50% of the mixture weight is
made up of grains having diameters over 50 μ and about 25% is composed
of grains having diameters smaller than 20 μ (to which accrues over
75% of the total grain area in the mixture).

In the light of these data, the importance of analyzing process
kinetics in polydisperse mixtures becomes obvious. Such an analysis
may be constructed on the basis of the following simple considerations
[391, 393].

If the "coated" reagent consists of grains of initial sizes R_1,
R_2, ..., R_n and the rate of the process, being limited by diffusion of
the second reagent through the "coating" layer (i.e., the product
layer), is practically independent of the rate of external diffusion

- 324 -

toward the surface of this layer, then each fraction of the "coated" reagent undergoes transformation independently of the other fractions.

In this case, the conversion kinetics of the individual fractions may be expressed by the equations

$$I_1 \quad 1 - \frac{2}{3}a_1 - (1-a_1)^{\frac{2}{3}} = KR_1^{-2}\tau,$$

$$I_2 = 1 - \frac{2}{3}a_2 - (1-a_2)^{\frac{2}{3}} = KR_2^{-2}\tau,$$

$$\cdots \cdots \cdots \cdots \cdots \cdots$$

$$I_n = 1 - \frac{2}{3}a_n - (1-a_n)^{\frac{2}{3}} = KR_n^{-2}\tau,$$

where R_1, R_2, ..., R_n express the radii of spheres equivalent in size to the over-all average grain in the fraction.

Clearly, having determined the value I_1 of some single fraction, we may compute the I_n of any other n^{th} fraction for the same conditions (t^0, τ and others) from the formula

$$I_n = I_1\left(\frac{R_1}{R_n}\right)^2. \tag{182}$$

The total fraction of reacted "coated" reagent after a time τ will obviously be

$$a = y_1 a_1 + y_2 a_2 + \ldots + y_n a_n, \tag{183}$$

where y_1, y_2, ..., y_n are the weight fractions of grains of the respective average sizes R_1, R_2, ..., R_n in the total quantity of this reagent in the mixture.

Solution of the problem as a whole now reduces to the following. On the basis of experiments with grains of some given size (or of a single narrow fraction), we compute the value of the constant K for specified conditions (temperature, etc.) of the reaction.

From the known K and R and the assigned values of the process time τ, we compute the values of the functions I from the expression

$$I = KR^{-2}\tau.$$

Further, using the semilogarithmic diagram of Fig. 76 (which should be constructed on a large scale for this purpose), we find

G_1, G_2, ..., G_n from the resulting values of I_1, I_2, ..., I_n.

Finally, we use Equation (183) to find the total degree of conversion G of the coated reagent after a time τ in the polydisperse mixture.

Thus, a few operations enable us to find G as a function of τ for a mixture of any granulometric composition.

The accuracy of the results obtained depends, of course, on the range of grain sizes within the limits of the individual fractions: it will be the higher the narrower the fraction.

The above exposition equips us to dwell upon certain problems of selecting efficient granulometric composition in crystalline mixtures for practical purposes.

As we know, the minimum porosity is reached with relatively large surfaces of direct contact between granules when the range of grain sizes in the mixture is quite wide. In accordance with this, and in view of certain other considerations that carry weight in technology, e.g., refractory technology, wide grain-size ranges are deliberately maintained. Various experimentally based grain-composition recommendations for raw mixtures that have been based on this proposition have come to light (see, for example, [49, 296]).

The use of these recommendations is naturally limited to processes whose rate and results are independent of the rate of internal diffusion.

The occasionally encountered extensions of such recommendations to processes of chemical conversion in solid mixtures whose rates and results depend on the rate of diffusion into the interior of granules are usually unjustified for at least two reasons:

1) in the overwhelming majority of practical cases, the area of the surface of direct contact between granules and the rate of ex-

ternal diffusion toward the surface of the "coated-reagent" granules do not limit the rate of the chemical reaction in the solid mixture;

2) where there is an essential difference between the grain sizes of a single mixture, the difference in the degree of conversion of various grains (or fractions) in it may run to tens of percent; when some (fine) grains have been converted 100% into the product, other grains (large ones) may be converted by only 10-15%; when the process of conversion of the coarse grains subsequently goes to completion over a relatively long span of time, the fine grains act as ballast.

From this standpoint, it is naturally advisable in conducting processes that are limited by internal diffusion to maintain a relatively narrow range of grain sizes by extracting rather fine fractions.

An interesting property makes its appearance in this case if the process takes place in the presence of accelerating additives which act as fluxes. This problem is considered in §2 of the present chapter, which is devoted to accelerators for these reactions.

Earlier in this section, we have been concerned almost exclusively with the diffusion region of the reaction and the grain size of the reagent that becomes coated with the product as the reaction advances. It does not, of course, follow from this that the grain size of another reagent or other reagents is not of essential importance. The investigations of Budnikov [1, 384, 394], Berezhnoy [293, 395], Ginstling [231], Kaynarskiy [396] and many other authors indicate that the reaction rate depends heavily in certain cases on the grain size of the diffusing component.

For example, in investigating the reaction of magnesium oxide with quartz in the respective proportions of 60 and 40% in the mixture, at a temperature of $1620°$ and with a process time of 2 hours, Berezhnoy obtained the results shown in Table 32.

TABLE 32

Influence of Grain Size of Quartz and Periclase
on the Rate of the Reaction Between Them [293, 397]

1 Размер зерен в мм		4
2 кварца	3 окись магния (периклаз)	Доля связанной окиси магния в %
0÷0.1	0+0.1	96
2÷3	0÷0.1	56.6
0÷0.1	2÷3	14.3

1) Grain size in mm; 2) quartz; 3) magnesium
oxide (periclase); 4) fraction of bound mag-
nesium oxide in %.
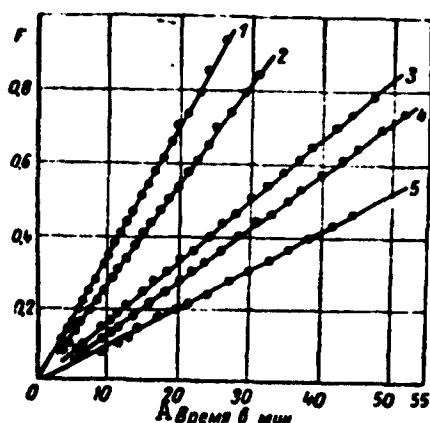
Fig. 77. Kinetics of reac-
tion between calcium car-
bonate (with grain size
$r_{CaCO} < 0.030$ mm) and
molybdenum oxide with
$[CaCO_3]:[MoO_3] = 15$ at a
temperature of 620°.
Grain sizes of MoO_3 (in
mm): 1) 0.052; 2) 0.064;
3) 0.119; 4) 0.13; 5)
0.153. A) Time in minutes.

These results indicate quite con-
vincingly the influence exerted by the
grain sizes of the two reagents on the
rate of the process under the conditions
studied by the author.

In studying the reaction of molyb-
denum oxide with calcium carbonate
under various conditions, Ginstling and
Fradkina [231] observed a significant
dependence of the process rate on the
grain size of the two reagents. With a
relatively large grain size of the
coated reagent ($CaCO_3$) and a small
grain size of the MoO_3, the rate of the
process was determined by internal dif-
fusion (see Fig. 71) and depended on the $CaCO_3$ grain size. Under other
conditions, when the kinetics of the over-all process was controlled
by sublimation of the molybdenum oxide (Fig. 77), the reaction rate
was a function of the MoO_3 grain size.

Figure 78 and Table 33 show the results of the synthesis of

gahnite from zinc oxide (ZnO 99.84%) and alumina (Al_2O_3 99.31%), as studied by Kaynarskiy and Sidorov [396] with 1:1 proportions between them at temperatures of 800 and 1200°.

These results also confirm the heavy dependence of the process rate on the grain size of the diffusing (in this case, the sublimating) reagent: when the zinc-oxide grain size is approximately doubled (from 70-90 to 150-200 μ), the rate constant changes by a factor larger than 4 (for example, from $0.067 \cdot 10^{-6}$ to $0.015 \cdot 10^{-6}$). Here we are concerned with a reaction between extremely fine-grained alumina and coarse-grained zinc oxide. Under these conditions, just as in the experiments noted earlier [231], the process rate is obviously limited not by the rate of internal diffusion of the zinc oxide through the very thin layers of gahnite, but by the rate of its sublimation, or not only by the rate of this diffusion, but also by the rate of sublimation.
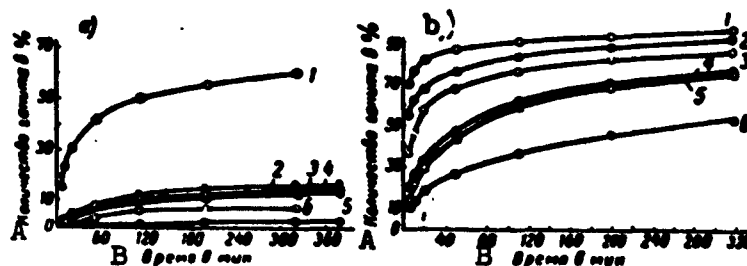
Fig. 78. Reaction kinetics of zinc oxide with aluminum oxide at temperatures of a) 800°; b) 1200°. Grain sizes of ZnO and Al_2O_3 (in μ) respectively as follows: 1) 2 to 6, 2 to 6; 2) 2 to 6, 70 to 90; 3) 2 to 6, 150 to 200; 4) 70 to 90, 2 to 6; 5) 70 to 90; 6) 150 to 200, 2 to 6. A) Quantity of gahnite in %; B) time in minutes.

This makes clear the great importance of the ZnO grain size under these conditions.

It is difficult to go along with the other explanations offered by Kaynarskiy and Sidorov for their observations, and, in particular,

TABLE 33

Averaged Rate Constants of Reaction of Zinc Oxide with Alumina

Размер зерен в μ		K·10⁹	
ZnO	Al₂O₃	при температуре реакции в град.	
		800	1 200
70—90	70—90	0,002	4,95
2—6	70—90	0,088	27,46
2—6	150—200	0,047	15,26
70—90	2—6	0,067	5,54
150—200	2—6	0,015	1,29

* Calculated by the Zhuravlev formula [336].

1) Grain size in μ; 2) at reaction temperature in degrees.
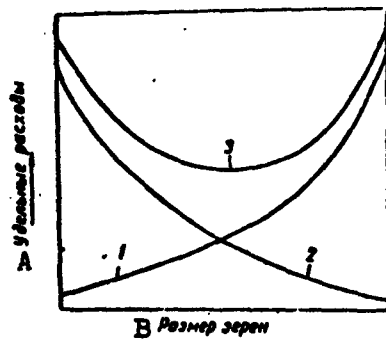
Fig. 79. Nature of unit costs as functions of grain size. 1) Heating of mixture; 2) grinding of components; 3) sum of costs. A) Unit costs; B) grain size.

with the limitation of the part taken by the gaseous phase to the initial period of the reaction that they studied [396]: with a unit ratio $ZnO:Al_2O_3$ in the mixture, the considerable difference between their specific gravities, a ZnO grain size that exceeds that of the Al_2O_3 by several hundred per cent, and the non-ideal mixing makes it inconceivable to us that the reaction between them should take place at the rates represented in Fig. 78 without participation of a gaseous phase, i.e., without sublimation of the ZnO.

Thus, in accordance with the general conceptions set forth in Chapter 5 for the kinetics of reactions in solid mixtures, the rates of these reactions may depend on the grain sizes of all initial components and any combination of them.

In isolated (extreme) specific cases, the reaction rate may depend on the grain size of some single component. Under practical conditions, this component is most frequently the substance coated by the

product layer during the reaction. However, many examples that deviate from this situation could be cited.

In conclusion, let us dwell for a moment on one consideration of a practical nature.

Under industrial conditions, an increase in the area of a reaction surface and a decrease in the average path of internal diffusion or in grain size not only favorably affects the output of the apparatus (furnace) in which the mixture is being roasted and the quality of the roasting product, but, as we know, also opens possibilities for lowering the process temperature and the specific consumption of power or fuel. On the other hand, reducing the grain size entails an increase in the cost of grinding and frequently brings complications in the matter of dust control.

The question of the rational degree (rational limit) of grinding the raw mixture components arises in this connection. Resolution of this question must apparently be achieved by technical-economic analysis.

The specific costs of producing a product of roasting are naturally a certain function of the degree to which the initial reagents are ground fine. The minimum of this function, the form of which may be found for each given process, will give the value of the economically optimal grain size.

A diagram of a simplified graphical solution of this problem is presented in Fig. 79. Assuming certain unit costs in first approximation (e.g., the cost of raw material per unit of product) that do not depend on the extent of grinding, we may envision the following pattern. The specific cost of heating the reaction mixture increases in accordance with a definite law that is characteristic for the process in question (curve 1), while the cost of grinding its components di-

minishes (curve 2) with increasing grain size. The minimum on curve 3, which expresses the sum of these costs for each grain size, permits a judgment as to the economically most efficient degree of refinement.

§2. CHEMICAL COMPOSITION OF MIXTURE. ACCELERATORS

The rate of a reaction in a solid mixture naturally depends on its chemical composition or, in other words, on the content of reagents and inert admixtures in it.

However, in contrast to reactions in liquid phases and gases, we are not concerned in this case with the nature of the connection between reaction rate and bulk concentration of reagents in the chemist's usual sense. In the case of a reaction in a crystalline mixture, the mechanism by which its chemical composition influences the kinetics of the process is usually found to be much more complex.

Let us first consider the conditions that arise in mixtures that do not contain chemically inert admixtures. Various cases are possible here, depending on the quantity of the compounds formed by the mixture components, the proportions between the average grain sizes of the various components, their physical properties, shape, surface properties, and so forth.

In the simplest case, in which only one compound AB is formed between the components A and B in a practically monodisperse mixture of them, which would consist of grains of the same shape and strength [sic], a change in the ratio A:B in the mixture changes the thickness of the product diffusion layer that forms during the reaction process (if the specific gravities of components A and B are different), the reaction-surface area and the cross-sectional area of the diffusion flux. Here, an increase in the content of, for example, the "coated" component in the mixture naturally reduces the total thickness of the product diffusion layer and this affects the kinetics of the

process accordingly [398].

The experimental data of many authors [398-400 and others] confirm this statement.

In cases where A and B have different grain sizes, the rate of the process may change variously with changes in the A:B ratio, depending on the mobility difference between the components A and B or elements of their lattices. If component A is the "coated" component and its grain size is larger than that of B, then an increase in the content of A in the mixture will have a particularly sharp effect on the process rate (an increase in the content of "coated" component in the mixture will be reflected therein to a considerably lesser degree). In the light of the above, it becomes clear that the occasionally encountered (see, for example, [400]) explanation for the process-kinetics changes that arise in the case described here in terms of increased initial contact-surface area between granules is inadequate, since it does not take full account of the diffusion conditions.

Let us now turn to an analysis of the influence exerted by natural impurities in crystalline reagents and accelerating additives (the so-called mineralizers) introduced deliberately into their mixtures upon the reactions under consideration. In this case, we shall be concerned with impurities and additives that are chemically inert with respect to the reaction mixture, i.e., that do not, for all practical purposes, participate in chemical reaction with the mixture's initial components, nor with its intermediate and final products, under the conditions under which the process is being run.

The presence of each such impurity or additive changes the conditions of the reaction as compared with those prevailing when it takes place in a mixture of absolutely pure reagents and, naturally, influences the reaction, particularly its rate and the properties of

the product obtained. Depending on the properties of the reagents and the impurities (or additives) as well as on the conditions of the process, this influence may take widely varying forms as regards both nature and direction and intensity.

Barta [62] lists fifteen different ways in which mineralizers act on reactions between solids and classifies all mineralizers into three large groups, those influencing

1) the formation of seeds (centers of crystallization);

2) rate of crystallization (especially by changing the viscosity of the system and the dissipation of heat from it);

3) the lattices and, accordingly, the properties of the crystalline solids (including the so-called superficial, structural and diffusion mineralizers).

In evaluating the possible effects of impurities and artificial additives on reactions in mixtures of solids, it must be remembered that all of the "elementary" processes or stages making up these reactions, as enumerated earlier on pages 160 and 161, are objects of this influence. The change in conditions brought about by an impurity or additive may affect various "elementary" processes or stages of the reaction in various directions (e.g., by promoting or inhibiting their progress) and to different degrees (for example, it may affect one process markedly and have practically no noticeable effect on others). The resultant effect of an additive (or impurity) on a reaction, whether its effects on individual stages work in the same direction or in different directions (are positive or negative), depend: a) on the relationship between the activation energies and between the rates of the individual stages in the absence of the mineralizer (or impurity) and b) on the comparative effectiveness of its influence on the various stages. This resultant action is obviously determined

primarily by the influence of the mineralizer (impurity) on the limiting stage (the limiting "elementary" process) of the reaction.

It is clear from the above that the over-all influence of a "mineralizer" on a given specific reaction in a solid mixture may be understood and even predicted with high probability given understanding of the direction, mechanism and comparative effectiveness of the action of this mineralizer on the individual stages of the reaction.

Study of the mineralizer from this point of view [401, 402 and others], investigation of the effectiveness and mechanism with which the impurity acts on the "elementary" diffusion processes [88, 103, 110, 111], polymorphic transformation [403-405], sintering [83, 132, 135-140, 146, 406, 407], dissociation [405], fusion, etc., open the way to theoretical generalization and the achievement of worthwhile practical results in this field.

For example, analysis of the mechanism by which fluxing additives influence the diffusion stage of reactions between solids [402] enables us to account for the influence of small quantities of such additives on these reactions, the existence of an optimum content of the additive in the mixture and a certain temperature interval in which it acts effectively, the varying behavior of the additive at different degrees of conversion of the initial substances into the product, the link between the grain size of the initial mixture and the effectiveness of the additive, and many other phenomena.

The presence of a substance that forms a more or less low melting mixture with one or more of the charge components greatly increases the contact area between the reagents, the rate of diffusion, and (if the process is taking place in the diffusion region) the rate of the over-all process.

If, for example, we add to a mixture of reagents A + B a flux

together with which a certain (perhaps very small) quantity of reagent A passes into the liquid phase at a given temperature, then the latter [reagent A] will diffuse at a high rate through the layer of the product AB toward particles of the second reagent B and react intensively with them, thereby increasing the thickness of the layer of reaction product AB. To the extent that A, on reacting with B, is converted into AB and thereby eliminated from the liquid phase, a corresponding quantity of it quickly melts, diffuses through AB, reacts with B, and so forth, until the quantity of A in the mixture is sufficient to maintain all of the flux in the liquid phase at the temperature in question.

In this way, i.e., in accordance with scheme XII (page 202), a very small quantity of flux may progressively convert a large quantity of reagent to the liquid phase and assist in intensifying the reaction.*

From the time at which the quantity of unreacted component A in the mixture becomes sufficient to hold all of the flux in the liquid phase, the flux crystallizes progressively as the reaction advances in the diffusion layer of product AB and about it, thereby inhibiting the diffusion process.** The extent of this inhibition depends on the content of flux in the mixture.

Thus, depending on the quantity of inert flux introduced into the mixture, the positive part that it takes at the beginning of the process may be nullified and then become negative as the reaction progresses.***

The acceptable amount of such a process accelerator may be computed in approximation from the diagram of state of the system involved, as a function of the desired degree of conversion of the reagents into the product at the temperature in question.

The effectiveness of use of an accelerating additive of this kind is not the same under different conditions. The effective temperature range of such an additive is limited on the one hand by the temperature t_1 at which some component (or components) of the reaction mixture melt with the additive and, on the other hand, by the temperature t_2 at which a liquid phase appears in such a mixture in the absence of the additive (Fig. 80).

As a result, for example, the influence exerted by different additives to the reaction mixture upon a given process at a given specific temperature may differ widely.

The results of References [398, 408-411] (see Figs. 81-85) may serve as an illustration for the above statements. It was established in these and many other studies that a content of 1-3% of a fluxing additive in the crystalline mixture may be sufficient to intensify many reactions greatly, and that the introduction of the additive into the mixture may, in certain cases, first accelerate and then inhibit the process.

It has been shown for a number of reactions that the range of effectiveness of the additive is restricted to certain temperatures (see, for example, Fig. 81). It has been established, for example, that under practical conditions, calcium fluoride greatly accelerates the reaction in which the minerals of cement clinker form at temperatures below $1300°$, i.e., before the liquid phase appears in the CaO-Al_2O_3-Fe_2O_3-SiO_2 system, which corresponds to the composition of the raw-material mixtures used in the production of Portland cement.

Examination of the usual relative positions of the kinetic curves of the process with and without mineralizers (Fig. 86) shows that in comparative study of the effect of various mineralizers on a process, it is not admissible to restrict ourselves to any single value of the
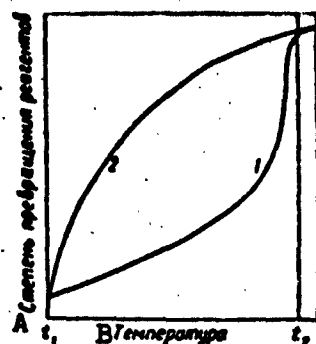
Fig. 80. General nature of effect of fluxing mineralizer at various temperatures. 1) Without mineralizers; 2) in presence of mineralizer. A) Degree of conversion of reagents; B) temperature.
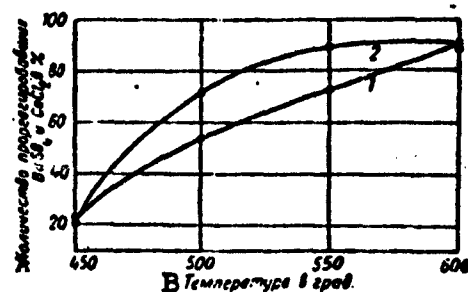
Fig. 81. Reaction of barium sulfate with calcium chloride (1:1). Yield of products after 58 minutes. 1) In absence of NaCl; 2) with 3% content of NaCl in initial mixture. A) quantity of reacted $BaSO_4$ and $CaCl_2$ in %; B) temperature in degrees.
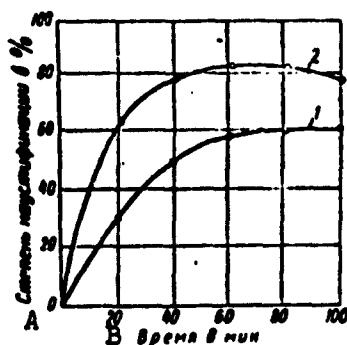
Fig. 82. Rate of caustification of soda by ferric oxide in the presence and absence of NaCl in the mixture, with the $[Fe_2O_3]$: $[Na_2CO_3]$ ratio = 1.5 at a temperature of $770°$. 1) In the absence of NaCl; 2) with 2.8% NaCl on weight of Na_2CO_3. A) Degree of caustification in %; B) time in minutes.
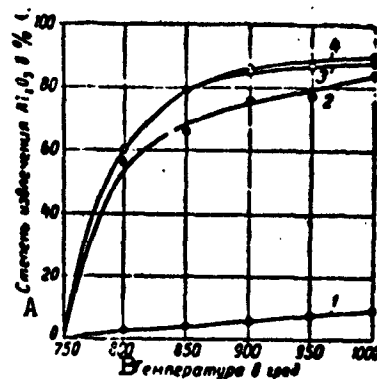
Fig. 83. Degree of extraction of aluminum oxide from sintering lime-nepheline charge with various soda contents and process temperatures; sintering for 60 min. 1) in absence of soda; 2) 3%; 3) 6%; 4) 10% of Na_2CO_3 on weight of nepheline. A) Degree of Al_2O_3 extraction in %; B) temperature in degrees.
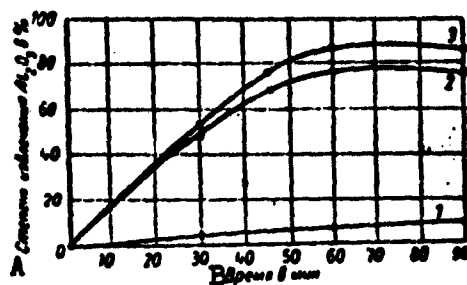
Fig. 84. Degree of extraction of aluminum oxide from lime-nepheline charge being sintered at 950°, with various soda contents: 1) In the absence of soda; 2) 3%; 3) 6% Na_2CO_3 on weight of nepheline. A) Degree of Al_2O_3 extraction, in %; B) time in minutes.

Fig. 85. Influence of fluorides on the reaction process between mixed calcium oxide and silicon dioxide, during 1 hour. 1) In absence of fluorides; 2) with CaF_2; 3) with AlF_3; 4) with MgF_2; 5) with NaF, each in quantity of 0.95% F on mixture. A) Fraction of CaO bound in %; B) temperature in degrees.

reaction time in all experiments.

It is obvious that in limiting ourselves to data on the degree of interaction of the reagents without and with mineralizers for any given value τ of the reaction time, we may arrive at different conclusions, depending on the value of τ selected. This conclusion is not adequate as a basis for judgments concerning the effectiveness of the action of any one of the mineralizers on the process, and much less so for comparative characterization of the mineralizers. This can be done only as the result of detailed study of the process kinetics.

With the mechanism of the additive effect described above, the intensification of the process will naturally be the greater the greater the extent to which its rate is limited by the diffusion rate; other conditions the same, the effectiveness of the additive is symbatic to the thickness of the reaction-product diffusion layer and, naturally, to the grain size of the "coated" reagent (see, for example, Table 34). Hence the fineness and nonuniformity to which the reaction-mixture components are ground has less effect on the results of the process in the presence of such an additive than in its absence.
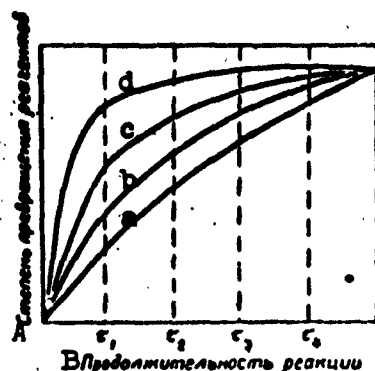
Fig. 86. Typical relative positions of kinetic curves of process:
a) Without mineralizers; b, c, d) in presence of mineralizers.
A) Degree of conversion of reagents; B) reaction time.

The influence of additives on the sintering process of crystalline solids is of great interest. Study of this process has established that it is strongly influenced by the composition, structure and properties of the liquid phase that arises in the system with participation of the additive [137, 138].

We note in conclusion that introduction of an additive (mineralizer) into the reaction mixture may, instead of causing fluxing, result in the formation of solid solutions or a change in the composition

TABLE 34

Reaction of Soda With Ferric Oxide With Various
Grain Sizes, With and Without Fluxing Additive
[398, 408]

1 Содержание добавки NaCl в смеси в % вес. от Na₂CO₃	2 Степень каустификации соды в % при размере зерен окиси железа в мм		
	0,06—0,08	0,17—0,25	0,6—8
0	53,2	18,9	9,2
0,8	88,6	26,8	22,5
2,2	88,6	73,8	60,1

1) Content of NaCl additive in mixture in % by weight of Na_2CO_3; 2) degree of caustification of soda in % for the following ferric-oxide grain sizes in mm.

of such solutions as a result of significant "opening up" of the crystal lattices (as is the case, for example, with formation of interstitial and subtractional solid solutions). This fact, the significance of which will depend on the ratio between the radii of the ions in the system with the additive and their charges, also has a

- 340 -

certain effect on the rates of certain "elementary" processes composing the reaction, and, in particular, on the diffusion and sintering rates.

In general, an impurity or additive in a crystalline mixture may function either to stabilize its composition or the composition of the products formed in it or as an accelerator or retarder of the processes that take place when such a mixture is heated.

§3. TEMPERATURE

Boltzmann's law, which describes the energy distribution of molecules in matter, permits us to establish, in general form, the nature of the relationship between the rate of a physical or chemical process and temperature:

$$N_i = \frac{N}{z} e^{-\frac{E_i}{kT}},$$

where N is the total number of molecules, N_i is the number of molecules with an energy E_i, k is Boltzmann's constant and z is the sum of states, the distribution function.

The form of the equation for the energy distribution of the molecules depends on the kind of problem, although the presence of the factor $e^{-Q/RT}$, which is known as Boltzmann's factor, is always characteristic for this distribution. In accordance with this, the rate constant of a reaction in a crystalline mixture is expressed by the equation

$$k = A e^{-\frac{Q}{RT}}, \tag{34a}$$

in which the quantities A and Q may take on different physical senses and values in accordance with the limiting stage (limiting "elementary" process) of the reaction.

In cases where the process is limited by the actual chemical reaction, the preexponential factor A = Pz_0, where P is the probability

or steric factor, z_0 is the number of double (for a bimolecular reaction) collisions between the reacting particles, and Q is the activation energy for the chemical event, which depends on the bonding forces between the particles of each of the initial substances and on the forces of repulsion between particles as they approach one another (for heterogeneous processes, a group which includes reactions in crystalline mixtures, Q is the apparent energy of activation).

If the process takes place in the diffusion region, then its rate is limited by the coefficient of diffusion $D = Ae^{-Q/RT}$, where the value of A depends on the vibration frequency of the structural elements (e.g., atoms) of the crystal lattice and the average distance between their neighboring equilibrium positions and Q is the "opening" energy of the lattice, which depends on the bonding forces between its structural elements (pages 18-22).

If the "controlling" stage of the process is recrystallization, sublimation, adsorption, or the like, then A and Q depend accordingly on other factors as well.

Taking logarithms in Expression (34a), we obtain the Arrhenius equation

$$\ln K = \ln A - \frac{Q}{RT}$$

(184)

or, converting to common logarithms and assuming that A and Q do not vary with temperature, we obtain the equation of a straight line,

$$\lg K = b - \frac{a}{T}.$$

(184a)

where $b = \log A$ and $a = Q/2.303 \ R = Q/4.575$.

Using the experimental values of K for various temperatures to plot a diagram of log K vs. 1/T (Fig. 87) in which the slope of the line is a, it is easy to determine the numerical value of the apparent activation energy of the process. The most widely used method

Fig. 87. Rate constant of reaction as a function of absolute temperature. 1) log K.

for determining this energy also reduces to this.

Table 35 lists values of Q for certain reactions in mixtures of crystalline solids. The rate changes of the corresponding reactions as functions of temperature may be computed from the data of this table.

Actually, more rigorous analysis of this problem indicates that for a number of reasons. (see, for example, §1 of Chapter 2) the values of $\underline{a}$ and $\underline{b}$ and, in particular, the value of the apparent activation energy Q, which determines the quantity $\underline{b}$, in Equation (184a) may change for reactions in crystalline mixtures as the temperature changes, and do so in some cases over a rather wide range.

It follows directly from Equation (34a) that the higher the activation energy of this process, the more widely will the rate of the process vary with temperature.

Numerical characterization of the reaction rate constant as a function of temperature naturally involves the nature of the limiting stage of the reaction. In the case of a diffusion process, which is usually characterized by a small activation energy, its rate changes relatively slowly with temperature: by 10-40% as the temperature changes through 10°. In cases where the process is limited by the actual chemical stage, on the other hand (a situation rarely encountered in intercrystalline reactions under practical conditions), the temperature dependence of reaction rate according to the Arrhenius equation is quite pronounced: a 10° temperature increase increases the reaction rate by a factor of 2-4 or more.

The considerations set forth above apply to an isothermal course

TABLE 35

Values of Activation Energy for Certain Reactions in Solids

1 Реакция	2 Условия	3 Q ккал/моль	4 Источник
$MgO + Al_2O_3 \rightarrow MgO \cdot Al_2O_3$	—	41,1	[569]
$MgO + TiO_2 \rightarrow MgO \cdot TiO_2$	—	41,1	[569]
$3MgO + 2Ag_3PO_4 \rightarrow Mg_3(PO_4)_2 + +6Ag + O_2$	6 Таблетированная порош-кообразная смесь	61,0	[340]
$MgO + Ag_2SO_4 \rightarrow MgSO_4 + 2Ag + +\frac{1}{2}O_2$	7 То же	61,0	[340]
$MgO + Mg_2P_2O_7 \rightarrow Mg_3P_2O_8$	8 Взаимодействие между таблетками	82,0	[223]
$CaO + Al_2O_3 \rightarrow CaAl_2O_4$	Таблетированная порош-кообразная смесь	43,3	[336]
$CaO + SiO_2 \rightarrow$	7 То же	54,0	[261]
$CaO + SnO_2 \rightarrow CaO \cdot SnO_2$	•	85,0	[569]
$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2$	•	86,0	[243]
$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2$	5 Порошкообразная смесь	31,4	[231]
$BaCO_3 + SiO_2 \rightarrow$	Таблетированная порош-кообразная смесь	56,0	[243]
$BaCO_3 + TiO_2 \rightarrow$	7 То же	62,5	[569]
$BaCO_3 + WO_3(1:1) \rightarrow BaWO_4 + +CO_2$	•	44,0	[243]
$BaCO_3 + WO_3(1:1) \rightarrow BaWO_4 + +CO_2$	•	32,1	[243]
$ZnO + Al_2O_3 \rightarrow ZnAl_2O_4$	8 Взаимодействие между таблетками	98,0	[224]
$PbO + SiO_2 \rightarrow$	Таблетированная порош-кообразная смесь	12,8	[261]
$PbO + PbSiO_3 \rightarrow Pb_2SiO_4$	7 То же	61,3	[261]
$PbO + PbSiO_3 \rightarrow Pb_2SiO_4$	8 Взаимодействие между таблетками	114,0	[223]
$2PbO + Pb_2SiO_4 \rightarrow Pb_4SiO_6$	7 То же	180,0	[223]

1) Reaction; 2) conditions; 3) Q in kcal/mole;
4) source; 5) powder mixture; 6) tableted
powder mixture; 7) same; 8) reaction between
tablets.

of the reaction. However, the exothermic nature of most reactions in crystalline mixtures, combined with the relatively low heat capacity and thermal conductivity of the latter, may result in considerable

heating of the reaction mixture during the reaction. On the other hand, an increase in the temperature of the reagents (which quite probably differs from the temperature of the reaction space) as the reaction proceeds will naturally influence the reaction rate. Yander [333] attempted to take this into consideration on the basis of the following considerations in his description of the kinetics of the reaction that he studied (see page 239).

Denoting by the subscripts n and k the initial and final stages of the reactions, respectively, we may write

$$K_n = Ae^{-\frac{Q}{RT_n}} \text{ and } K_k = Ae^{-\frac{Q}{RT_k}}.$$

Then the following equation will apply at any moment during the reaction:

$$K = K_n \exp\left[-\frac{Q}{R}\left(\frac{T_n - T}{T_n \cdot T}\right)\right].$$ (185)

Assuming that the difference $T_n - T$ is proportional to the thickness x of the product layer and that the product $T_n T$ is in first approximation constant, we find that the rate constant of the reaction

$$K = K_n \cdot e^{-ax}.$$

If we now substitute this value of K in the equation

$$x^2 = 2K\tau,$$ (91a)

we find that

$$x^2 = 2K_n e^{-ax}\tau.$$ (186)

and since

$$x = R\left(1 - \sqrt[3]{\frac{100 - y}{100}}\right) = R(1 - \sqrt[3]{1 - a}),$$ (150)

then

$$\left(1 - \sqrt[3]{\frac{100 - y}{100}}\right)^2 = K_1 \exp\left[-c'\left(1 - \sqrt[3]{\frac{100 - y}{100}}\right)\right].$$ (187)

where

$$K_1 = \frac{2K_2}{R^\circ} \text{ and } c' = cR.$$

It should be noted in connection with this reasoning that with spherical, cubic and similar (nonlaminar) reagent-granule shapes, the difference $T_n - T$ is not a linear function of the thickness x of the product layer, if only for the reason that the value of x is itself nonlinearly related to the quantity of the materials that has reacted. Further, the heat radiation of the reaction mass, which is proportional, according to the Stefan-Boltzmann law, to the difference between the fourth powers of the temperatures of the more severely heated and less severely heated solids, will also naturally affect the value of $T_n - T$. Finally, according to what we said earlier (§6 of Chapter 5), a fundamental change in the kinetics of the process during time is possible even when its progress is isothermal; this is the more likely to be the case when the temperature of the reaction mixture changes, as discussed earlier.
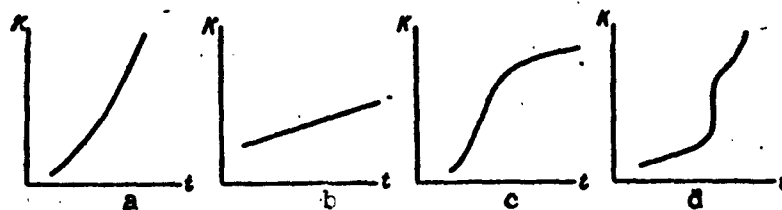
Fig. 88. Nature of change in reaction rate as a function of temperature under various conditions. K is the rate constant of the reaction and t is the temperature. a) Region of chemical kinetics; b) diffusion region; c) progressive transition from a to b; d) relatively sharp transition from b to a.

These circumstances naturally limit the applicability of Equation (187) to a rather narrow range of conditions; in the general case, it is highly approximate in nature.

In practice, and under industrial conditions in particular, reactions in crystalline mixtures actually take place quite often with
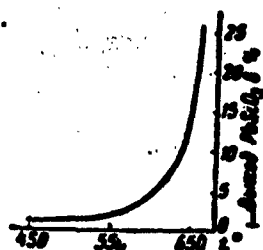
Fig. 89. Reaction
between PbO and
SiO_2 at various
temperatures [410].
1) Yield of $PbSiO_3$,
in %.
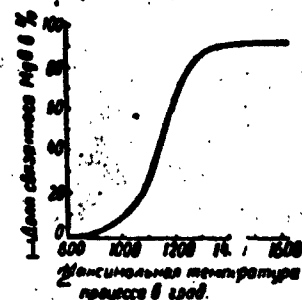
Fig. 90. Reaction
of magnesium oxide
with zircon at
various temperatures.
$\tau_{t_{max}}$ = 2 hours. 1)
Fraction of bound MgO
in %; 2) maximum pro-
cess temperature in
degrees.
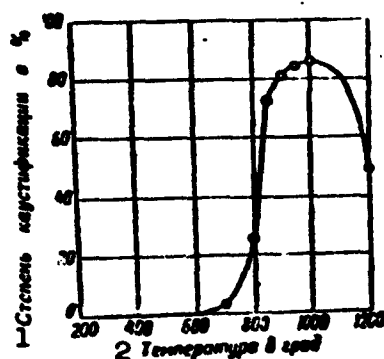
Fig. 91. Reaction of
soda with ferric oxide
at various temperatures
[411]. 1) Degree of
caustification in %;
2) temperature in de-
grees.
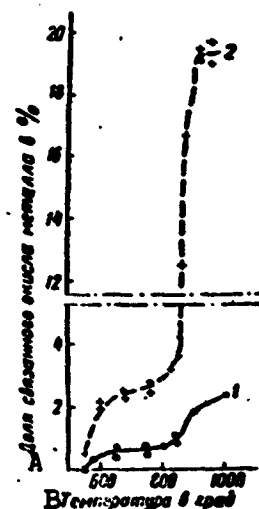
Fig. 92. Reaction
of NiO (1) and
Co_3O_4 (2) with
SiO_2 at various
temperatures. A)
Fraction of bound
metal oxide in %;
B) temperature in
degrees.

a gradual increase in temperature. This situation is by no means pe-
culiar to exothermic reactions; the reacting substances may gradually

- 347 -

become heated by an external source of heat.

Any of Equations (184-187) may be found inadequate to describe the process rate changes that take place here.

On the basis of considerations of the possible transition of the process as it proceeds from one region (e.g., that of chemical kinetics) into another (e.g., the diffusion region), we must accordingly acknowledge the possibility that the rate of a given process may vary in a different manner as a function of temperature in different temperature ranges. Usually, the attention given to this question in the study of solid-state reactions is inadequate.

The nature of the connection between reaction rate and temperature depends on the chemical and granulometric composition of the reaction mixture.

In the simplest cases of chemical and diffusion kinetics, the nature of this relationship is reflected by curves a and b, respectively (Fig. 88). In the case of a gradual transition of the process with rising temperature from the region of chemical kinetics into the diffusion region, the reaction rate constant varies following curve c. In the case of a relatively sharp transition of the process from the diffusion region into the region of chemical kinetics proper (such a transition may occur, for example, when part of the system reaches the melting point, with the resulting sharp drop in diffusion resistance), the rate of the reaction as a function of temperature is represented by curve d (see Fig. 88), and so forth.

A large quantity of experimental data corresponding to these curves is available. Certain examples of various experimentally established relationships for rate constant in crystalline mixtures as a function of temperature are given in Figs. 89-92.

§4. PRESSURE

It has been known since the experiments of Shpring [166], which were conducted during the eighteen-nineties, that severe enough compression of a crystalline mixture will affect the chemical reaction between its components. Briquetting a mixture of barium sulfate with sodium carbonate and other mixtures under a pressure of 6000 atmospheres, Shpring ran reactions in them at room temperature.

At the present time, the strong influence exerted by pressure on various processes in which powdered products (and mixtures in particular) undergo conversion is a well-known fact and one extensively exploited in industry. However, the mechanism and effectiveness of this action as a function of certain conditions that are of interest to the production engineer have not been investigated in many cases.

In considering this problem as related to reactions in solids, we may be concerned with: a) preliminary squeezing (press forming) of a powder mixture before the reaction is initiated in it and b) the conduct of the reaction itself under pressure. In the former case, the reaction kinetics may be affected by the shape change of the mixture granules and changes in their relative spatial arrangements, and in the second case, in accordance with the Le Chatelier principle, the equilibrium of the reaction may also be shifted.

The basic changes that occur in a powdered solid when it is compressed reduce to a change in the average distance between neighboring granules, changes in their shape, and changes in the total and contact surface areas. The nature of these changes may vary in accordance with the initial conditions: the mutual spatial arrangement of the grains, the ratio between their strengths, the presence and distribution of surface impurities, and the like (see §4 of Chapter 1).

Theoretical considerations indicate that regardless of the nature
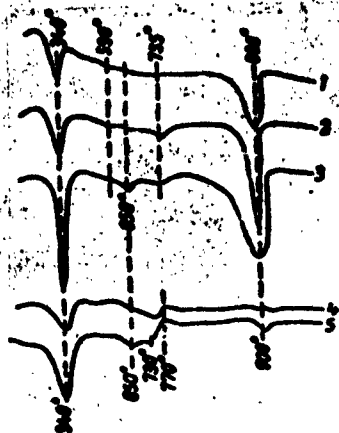
Fig. 93. Differential heating curves of mixtures of $CaCO_3$ with $MgSO_4 \cdot H_2O$. 1) 2:1 mixture, not pressed; 2) same mixture after five minutes of pressing at room temperature; 3) same, after eight hours of pressing at temperature of 300°; 4) 1:10 mixture, unpressed; 5) same mixture after five minutes of pressing at room temperature.

of certain of these changes, they may act on the reaction to one degree or another, and even push it in different directions, depending on the mechanism and conditions of the reaction. Thus, pressing a mixture to increase the surface of direct contact between granules in cases where the reaction takes place with participation of liquid or gaseous phases, i.e., when the second of the mass-transfer variants described above (§1 of Chapter 2) is in effect, may have little or no effect because of the relatively low value of mass transfer through the contact surface.

A change in the reaction kinetics of a powder mixture under pressure may occur chiefly as a result of its influence on the "elementary" processes of sintering, recrystallization and diffusion. Pressure has a particularly pronounced effect on sintering, which, in the opinion of many investigators, determines the "reaction capability" of such a mixture (we know that Tammann [412], Kordes [413] and others have identified the "reaction-onset" temperature of a powder with its sintering temperature).

Presintering briquetting of powders under one pressure or another is a procedure that has long been successfully applied in practice and described on many occasions in the literature (see, for example [48, 296, 414]). A relatively new process is the one in which sintering is conducted under pressure, which is also known as "hot" pressforming. In this case, the powdered solid (which has usually been briquetted
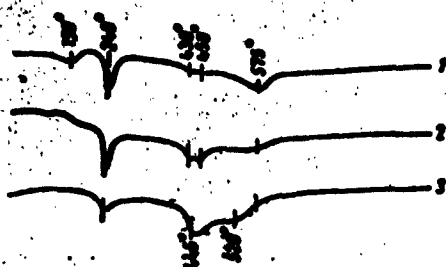
Fig. 94. Differential heating curves of mixtures of K_2SO_4 with Na_2SO_4. 1) Unpressed mixture; 2) same mixture after five minutes of pressing at room temperature; 3) same, after five repetitions of crushing and 5 minutes of pressing at room temperature.
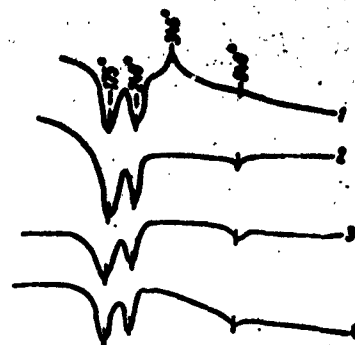
Fig. 95. Differential heating curves of mixtures of Na_2SO_4 with $CaSO_4 \cdot 0.5H_2O$. 1) Unpressed mixture; 2) same mixture after 5 minutes of pressing at room temperature; 3) same, after two repetitions of crushing and 5 minutes of pressing at room temperature; 4) same, after two repetitions of crushing and 6 hours of pressing at room temperature.

in advance) is subjected to the simultaneous effects of high temperature and pressure. References [415, 416] are devoted to the highly underdeveloped theory of this process. Merrey et al. [416] made the most detailed experimental investigation. The authors subjected specimens of beryllium, magnesium, calcium, aluminum, thorium and uranium oxides to pressforming in molds made from dense electrographite under a pressure up to 140 kg/cm^2 at temperatures up to 200°. Here, they established the possibility of obtaining compacts of high density and a very high rate of the sintering process under the conditions of "hot" pressforming. Thus, using a pressure of 140 kg/cm^2 and a pressforming temperature of 1500°, they obtained magnesium oxide with a bulk weight of 3.4 g/cm^3, beryllium oxide of 2.98 g/cm^3 at 1700°, cal-

cium oxide of 3.54 g/cm³ at 1800° and zirconium dioxide of 5.7 g/cm³ at 2000°. According to Merrey's calculations [416], the rate of compacting during sintering at a pressure of 70 kg/cm² is 105 to 178 times higher than in sintering under atmospheric pressure. Direct extension of these figures to the kinetics of the reactions in which we are interested, even in those cases where their limiting stage at atmospheric pressure is sintering, cannot be justified theoretically: any other of the "elementary" processes composing the reaction may assume the role of limiting stage when the sintering process is greatly intensified. However, accelerating the sintering of crystalline mixtures under pressure undoubtedly affects to some degree the conditions of diffusion in them and, in this way, the reaction rate as well.
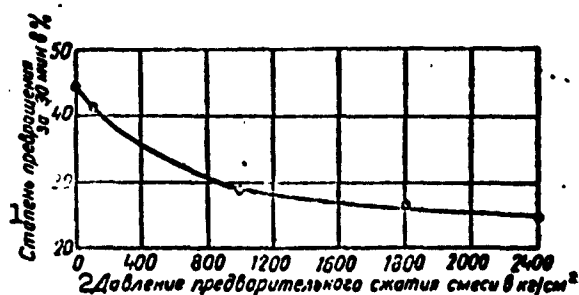
Fig. 96. Influence of prior squeezing pressure applied to mixture of copper sulfate and lead oxide on rate of reaction between them [237]. 1) Degree of conversion after 30 minutes, %; 2) pressure previously applied to mixture, kg/cm².

The beneficial influence of pressure on the conversion processes of solids has been described many times in the literature (see, for example, [1, 48, 214, 218]). One topic of description in these studies is the intensifying influence of pressure on chemical reactions in solids. An interesting investigation in this direction was carried out comparatively recently by Berg et al. [417]. The authors registered thermograms of powdered salt mixtures, free-poured and pressed at

TABLE 36

Influence of Pressforming Pressure on Synthesis of Magnesium Spinel

1 Характеристика образцов	2 Давление прессования в кг/см²		
	600	1200	6400
3 Объемный вес необожженных образцов в г/см³	1,39	1,64	2,6
4 Содержание свободной MgO в образцах, обожженных при 800°, в %	23,75	23,39	22,75
5 Выход шпинели после обжига при 800° в %	15,69	16,97	19,24

1) Description of specimen; 2) forming pressure in kg/cm^2; 3) bulk weight of unfired specimens in g/cm^3; 4) content of free MgO in specimens fired at 800°, in %; 5) yield of spinel after firing at 800°, %.

TABLE 37

Influence of Prior Squeezing Pressure Applied to Equimolar Mixture of Copper Sulfate and Lead Oxide on Rate of Reaction Between Them*

1 Давление предварительного сжатия смеси в кг/см²	2 Степень превращения сульфата меди в % в опытах			
	3 I серия	II серия	III серия	4 I—III серии (средняя)
0	45,0	44,5	43,7	44,4
100	43,5	—	39,0	41,2
300	39,0	38,2	35,0	37,4
1000	33,3	25,0	28,6	28,9
1800	28,7	27,5	25,3	27,2
2400	25,6	—	24,6	25,1

* The experiments were run at a temperature of 500° and with a reaction time of 30 min.

1) Prior squeezing pressure in kg/cm^2; 2) degree of conversion of copper sulfate in % in experiments of; 3) series I; 4) series I-III (average).

6000 atmospheres, as follows: a) $CaCO_3$ + $MgSO_4 \cdot H_2O$, b) Na_2SO_4 + $3K_2SO_4$, c) Na_2SO_4 + $CaSO_4 \cdot 0.5H_2O$ and others. The squeezing operation was performed at room temperature and at 300°. The appearance of new phases in the squeezing process was judged by the appearance of secondary effects on the thermograms. The results of the experiments (Figs. 93-95) show the appearance of 1-2% of new phases in the mixtures.

Thus, the difference in the behavior of unpressed and pressed

- 353 -

mixtures of the compositions studied and the occurrence of reactions in the pressed mixtures were undoubtedly established, although it is difficult to state that the appearance of new phases in these mixtures did not take place (at least in part) during the actual heating process when the thermograms were recorded.

Klyucharov and Levenshteyn [418] established the following pattern for the influence of squeezing pressure applied to a semidry initial mixture on the synthesis of magnesium-alumina spinel (Table 36).

The data of Table 36 indicate that an increase by a factor of 10 in the squeezing pressure applied to the mixture (from 600 to 6000 kg/cm^2) resulted in a significant change in the densities of the specimens (by 82%) under the conditions studied b, the authors, but increased the yield of reaction product by only 22%.

It follows from what was said earlier (pages 189 and 191) that when a reaction takes place in a solid mixture with participation of gases or liquid phases, its rate may not only fail to rise, but may even fall with increasing squeezing pressure on the initial mixture. This proposition has been confirmed experimentally by Pozin, Ginstling and Pechkovskiy [237] on the example furnished by the reaction of copper sulfate with lead oxide. The experiments were conducted at a temperature of 500°. Their results, which are presented in Table 37 and Fig. 96, indicate that the rate of this reaction drops off with increasing preliminary squeezing pressure applied to the reaction mixture.

Thus, depending on the composition of the reaction mixture, the physical properties of its components, the shape and sizes of their grains, and the nature and relative importance of the "elementary" processes composing the reaction, pressure may actually influence it

in different directions and to different degrees.

320

Obviously, profound systematic study of milling processes
with the objective of securing a radical increase in their
speed and economic efficiency, together with a considerable
increase in the attainable fineness is of no lesser im-
portance; as we know, research in this direction has recent-
ly been developing intensively.

Certain laws observed in grinding processes are extremely
complex. In view of this, and desiring to produce a result
that is useful for practical purposes, the actual mechan-
isms of such processes are usually simplified considerably
in theoretical analyses. Here, the simplifications (not
only of the grinding mechanism, but also of the general
concepts related to it) are sometimes so significant that
they result to a certain extent in loss of the essential
nature of the phenomena composing this process and deter-
mining its basic qualitative laws. This situation, which
is frequently encountered in work with crystalline solids,
has been pointed out convincingly in the work of Kuznetsov
[28, 29, 63], Rebinder [25-27] and other authors.

336*

It follows from this that the presence of a certain quantity
of impurities and moisture in solid reaction mixtures (which
are frequently governed by the composition of the natural
raw material) may have a positive effect on their conversion
rate if these impurities or moisture result in the formation
of a liquid phase in the system that improves conditions
for diffusion of one reagent toward another.

336**

Another reason for a progressive drop in process rate result-
ing from the use of a fluxing additive may be the gradual
transition of the flux from a liquid phase of composition A +
+ flux, AB + flux, and the like into the gaseous phase as a
result of crystallization of A, AB, and so forth, respec-
tively, and the resulting increase in resistance to diffusion.

336***

The mechanism and results of the action of a fluxing additive
in the case of transition into the liquid phase of a more
complex mixture (for example, additive — reagent A — reagent
B) under the conditions of the reaction are in principle
analogous to those described.

Manu- script Page No.	[List of Transliterated Symbols]
345	н = n = nachal'nyy = initial
345	к = k = konechnyy = final

Chapter 8

METHODS OF EXPERIMENTAL STUDY OF REACTIONS IN SOLIDS

The experimental study of reactions in solids involves considerable difficulty.

Obviously, securing reproducible research results requires sufficiently accurate reproduction of all conditions determining the course of the reaction. Nonconformity to this requirement will, as we know, result in considerable differences among the experimental results.

Exact reproduction of some of the conditions that exert an essential influence on reactions between solids (size and spatial distribution of the reagent granules, their content of impurities and of moisture in particular, distribution of temperature in the reaction mixture, and so forth) is frequently a rather difficult task.

As was noted earlier, such a reaction takes place in the overwhelming majority of cases at a rate that is of practical interest only at relatively high temperatures (frequently over a thousand degrees), and this is naturally a further obstacle to its study. Here, we frequently have simultaneous formation of several products possessing closely similar chemical properties. This renders separation of the products by selective solution extremely complex.

The similarity between the physical properties of the various substances, together with the complex structure, low symmetry and severe distortions of the crystal lattice, sometimes limits the possibility of investigating the solid reaction mixture by physical methods.

As a result, different methods are employed in different cases for study of reactions in solid mixtures. It is often possible to obtain reliable information on the composition and properties of the reaction products, and on the mechanism and kinetics of the process, only as a result of complex, comprehensive study of the process using several research techniques in parallel.

For these purposes, contemporary laboratory-research technique usually employs microscopy and microphotography, thermography, fluoroscopy and x-ray analysis, electron microscopy, selective solution, adsorption and, recently, radioactive indicators.

In the study, for example, of polymorphic transformations, crystal-morphological, crystal-physical and physicochemical research techniques are employed.

The crystal-morphological method consists in measuring crystals of the substance being investigated and establishing its syngony or one form or another of symmetry in a syngony. Ascertaining the syngony enables us to infer, in the majority of cases, the modification of the material, but measurement of the crystal angles is a rather difficult task and is possible in far from all cases.

Using crystal-physical methods, we determine the modification from its characteristic physical singularities: density, hardness, and optical, thermal, magnetic and electrical properties.

Finally, the physicochemical research methods are helpful in ascertaining the physicochemical stability conditions for the existence of a given modification or for its transition into another modification.

Contemporary laboratory and industrial technique has at its disposal a variety of other highly exact methods for determining the shape and size of powder grains, as well as their specific surface areas. These include adsorption, gravimetric, ultramicroscopic, elec-

tron-microscopic and other methods.

The electron-microscopy method enables us to determine the size and shape of particles whose dimensions lie in the range from 1 to 0.004 μ, while modern adsorption methods are quite applicable for grains from 20 to 0.002 μ.

Instruments for photometric measurement of grain size on the basis of suspension turbidity, which is a function of the grain surface area, have recently been developed and put to highly effective use.

To establish sufficiently precise, broad-range control over the rates of reactions between solids and the composition and properties of the products obtained, investigators engaged in study of these reactions have resorted frequently to grinding down the initial reagents, classifying them in accordance with grain size, injection of various types of additives into the initial mixtures to change the rate of the process, preliminary squeezing (tableting) of powdered reagents under various pressures, modern temperature-control methods, pressforming, applying gas pressure and vacuum during the reaction process, feeding currents of air and other gases into the reaction zone, conducting the reaction in the absence of direct contact between the solid reagents, and many other expedients and techniques that have been described in the literature.*

It is not the objective of the present monograph to go into detail on all of these methods and techniques for controlling reactions in solid mixtures. Consequently, we shall consider below only the most important methods for investigating such reactions.

§1. THERMOGRAPHY

As we know, thermography is concerned with study of the processes on the basis of the heat effects that accompany them. The heat effect may serve as a basis for judging the temperature conditions and in-

tensity of dehydration, dissociation, fusion, crystallization, chemical-reaction and other similar processes.

The heat effect may be expressed in the coordinates:

temperature versus time,

temperature versus the reciprocal of heating rate,

temperature difference (between the substance being investigated and a standard) versus time or the same temperature difference versus temperature.

The last two methods for expressing the heat effect are most satisfactory for study of reactions between solids.*
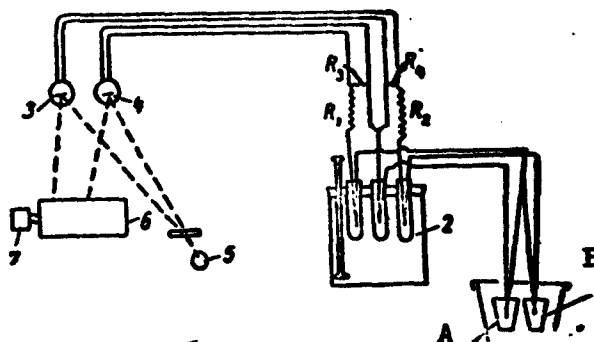
Fig. 97. Diagram of Kurnakov pyrometer with differential thermocouple. A) test object; B) standard. 1) Furnace; 2) thermostat for cold junctions; 3, 4) mirror galvanometers; 5) light source; 6) drum with photographic paper; 7) clockwork mechanism.

The automatically recording Kurnakov pyrometer with differential thermocouple (Fig. 97, [419]) is most frequently used for this purpose. One hot junction of this thermocouple is placed in the object of investigation, for example, in the reaction mixture, and the other in a reference substance (usually in aluminum oxide or magnesium oxide that has been roasted at t > 1000°) that does not undergo any noticeable transformations in the temperature range selected. The difference between the temperatures of the object and reference standard on heat-
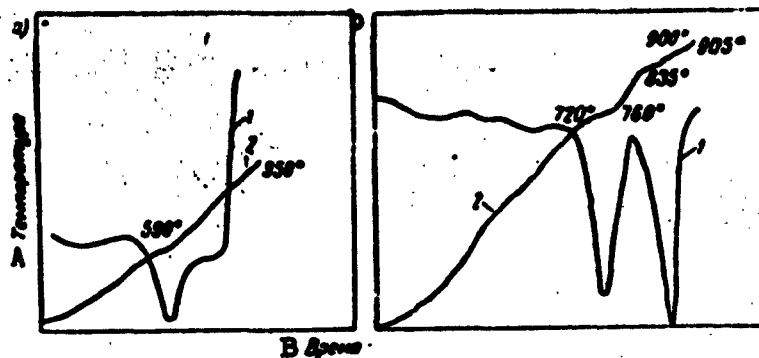
Fig. 98. Heating curves. a) Kaolinite; b) dolo-
mite. A) Temperature; B) time.

ing at the same rate — which arises due to the conversion heat effect
of the object of investigation — produces a difference between the
electromotive forces that are generated at the terminals A and B of
the differential thermocouple. This produces a deflection of the gal-
vanometer mirror and, accordingly, of the beam reflected by the mirror
onto photographic paper; since the paper is secured to a rotating drum,
the path of the beam traces out a line on it. The temperature of the
object is registered in the same way by a second galvanometer cut
into the circuit as shown in Fig. 97.

Development of the thermogram produces two lines: 1) the differ-
ential trace and 2) the direct trace (Fig. 98). The occurrence of a
process accompanied by a heat effect in the object of investigation
is judged from the break in curve 1, while curve 2 indicates the
temperature of this process.

The slope of curve 2 depends on the relationship between the
heating rate of the object and the speed with which the photopaper
drum rotates.

The differential-temperature-record method enables us to fix
processes that are accompanied by even very small heat effects. The
use of automatic registry makes it possible to obtain the research

results in the form of graphic and objective photographic documents.*

However, the accuracy of the results obtained depends on many of the experimental conditions. The errors that arise on fluctuations in the chemical and granulometric composition of the object, its properties (thermal diffusivity in particular), quantity, uniformity of mixing, heating rate and other conditions may be highly significant. As a result, conclusions concerning the temperature at which a given process takes place on the basis of thermograms must be made with great caution, supplementing the thermographic investigation with chemical, x-ray and microscopic studies.

§2. DILATOMETRY

Taking advantage of the jumpwise nature of the change in the thermal-expansion coefficient of a material on a phase transformation, we may conveniently observe the conditions for such transformations from a curve of temperature versus the length of a specimen of the
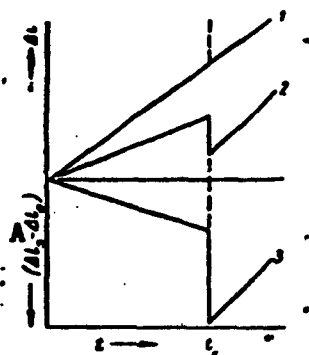
Fig. 99. Curves of temperature versus length change and temperature versus length-change difference. 1) Standard; 2) object; 3) difference between 1 and 2. A) $\Delta l_e -$ $- \Delta l_o$.

material being studied. It was by precisely this method that Le Chatelier [420] succeeded in 1889 in detecting for the first time the enantiotropic conversion of quartz from the β- into the α-modification, and establishing the temperature of this process.

Instruments of various designs known as dilatometers are used for investigations of this type. In a modern, highly sensitive differential dilatometer, the change in the length l_o of the object being studied on a change in temperature is compared with the change, under the same conditions, in the length l_e of a standard that does not undergo phase transformations in the

- 362 -

temperature region selected. Automatic registration of the difference between the length changes of the standard and the test object ($\Delta l_e -$ $- \Delta l_o$) enables us to establish the temperature t_x of the phase transformation from the break in the curve of Δl_o versus t and the vertical segment on the curve of ($\Delta l_e - \Delta l_o$) versus t (Fig. 99).

In the case of a two-phase mixture, we may, knowing the coefficients of linear expansion of the two phases, also form a closely approximate inference from the curve Δl versus t as to the relative content o. each of them in the mixture.

As we know, methods based on the change in the coefficient of volumetric expansion of materials and distinguished by high accuracy are widely used in practical physicochemical and physicomechanical research. In the chemistry of solids, however, these methods have highly limited applicability because of the difficulty involved in selecting a liquid medium stable at high temperatures for immersion of the substance being investigated.

§3 COMPLEX THERMAL ANALYSIS

In connection with the frequently encountered necessity of making comprehensive studies of solid-state reactions, methods for simultaneous complex investigation of solids that have recently undergone uccessful development are highly promising.

These methods include, for example, the so-called complex thermal analysis, which was developed and used in one variant by Voronkov (see Reference [421]) and in another variant by Keler and Kuznetsov [422, 423].

As we know, comparison of the differential heat-effect curve with curves showing the change in the volume and weight of the body being investigated under the same conditions is in many cases sufficient to form a basis for judgments as to the processes taking place

in it. In practice, however, such comparison is frequently unreliable as a result of the fact that even comparatively small differences in the experimental conditions (preparation of material, size of weighed specimen, heating rate, and so forth) may result in significant shifting of the temperature-versus-property curves.

The technique and apparatus for complex thermal analysis developed by Keler and Kuznetsov make it possible during the course of an experiment (for example, a reaction in a solid mixture) to register the thermal effects, volume change and weight change of the specimens simultaneously on the photopaper drum of the Kurnakov pyrometer. Here, the changes in the linear dimensions of the specimen (for which marks are made prior to the experiment) are transmitted to an optical system for photographic registration.

Side by side with the specimen for the shrinkage and heat-effect determinations, an identical specimen is suspended from a balance arm for determination of the weight change. The displacement of the beam from the arm mirror is also directed to the drum of the Kurnakov pyrometer.

Figure 100 shows the results of an investigation carried out by Keler and Kuznetsov [422] into the process in which barium carbonate reacts with titanium dioxide. Comparison of the curves obtained separately for TiO_2 and $BaCO_3$ (Fig. 100, A) with the heating curves of their mixture (Fig. 100, B) enables us to note the following:

a) retention of the $BaCO_3$ shrinkage in the mixture at temperatures from 600 to 800° and endothermic effects in its polymorphic transformations (at 835 and 970-980°) and

b) a drop in the dissociation temperature of $BaCO_3$ in the presence of TiO_2, the exothermic reaction forming barium titanate (at temperatures from 1100 to 1140°), which is accompanied by a sharp change in

- 364 -
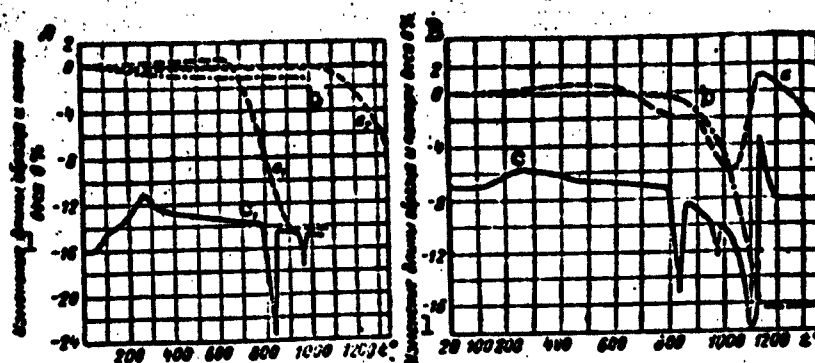
Fig. 100. Results of complex thermal investigation of process in which barium carbonate reacts with titanium dioxide. A) Initial reagents; a_1, b_1) $BaCO_3$; a_2) TiO_2; c) heat effect; B) formation of barium titanate; a) change in specimen length; b) weight loss; c) heat effect. 1) Change in specimen length and weight loss in %.

the volume of the material, and sintering of the barium titanate that has formed (when the temperature is raised to $1150°$).

The clarity of the results obtained provides a convincing description of the properties of the method described here.

§4. X-RAY DIFFRACTION STUDY

During the last 15-20 years, widespread use has been made of x-ray methods for structural, phase and dispersion analysis in studying reactions between solid substances. As we know, x-rays appear when a beam of cathode rays strikes a metallic obstacle (anticathode). Since the wavelengths of x-rays (from 100 to 0.1 A) are of the same order as the distance between the structural elements (for example, atoms) of a crystal lattice, such rays are diffracted when a beam of them strikes a crystal: each element of the lattice or, strictly speaking, each elcctron of its atoms, becomes a center of vibration when subjected to the action of the rays and emits x-rays in all directions. These waves display interference.

As was shown by Vul'f, the pattern formed when x-rays are
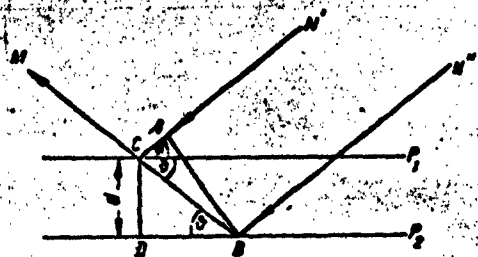
Fig. 101. Scattering of beam of x-rays by crystal [illustrating derivation of Equation (188)].

scattered by a crystal may be interpreted as the result of interaction of rays reflected by the ordinary laws of mirror reflection from mutually parallel planes of the crystal lattice.

Let a parallel beam of x-rays N', N", ... (Fig. 101) of wavelength λ strike a system of parallel planes P_1, P_2, ... of a crystal that are separated from one another by a distance $\underline{d}$. Forming a glancing angle ϑ with the planes P_1, P_2, and so forth, these rays are reflected at points B, C, and so forth, in the direction M. When the reflected rays interfere, they will naturally be amplified in those cases where the path difference $\Delta\underline{l}$ is a multiple of the wavelength.

Since the line AB ("beam front") is perpendicular to the direction of N' and N", then $\Delta\underline{l}$ = BC — AC.

We have from the right triangles CBD and ABC

$$BC = \frac{d}{\sin \vartheta}$$

and

$$AC = BC\cos 2\vartheta = \frac{d}{\sin \vartheta} \cos 2\vartheta,$$

from which

$$\Delta l = BC - AC = \frac{d\,(1-\cos 2\vartheta)}{\sin \vartheta} = 2d \sin \vartheta. \qquad (188)$$

According to the above, amplification of the beams takes place when

$$2d \sin \vartheta = n\lambda, \qquad (189)$$

where $\underline{n}$ is an integer (the order of the reflection).

The intensity of reflection is highest with n = 1 and diminishes rapidly as $\underline{n}$ increases.

If we direct a beam of "white" or heterogeneous (with regard to

- 366 -

wavelength) x-rays at a crystal C and place a photographic plate behind the crystal, a series of regularly spaced spots will appear on the plate after development (Fig. 102). The central spot O is the track of the x-rays that have passed through the crystal without deflection. The spots T_1 and T_2, which are arranged symmetrically about the central spot O, are the traces of rays that have been reflected by the atomic planes of the crystal and intensified by interference. The symmetry of the crystal may be determined from the arrangement of these spots and their intensity, i.e., we may establish the type of its space lattice. When monochromatic x-rays (consisting of waves of the same length) are directed at the crystal, they form, on striking one of the atomic planes, a central spot O representing the primary beam on the photographic plate and a weaker spot T, which is the result of reflection. It follows from Equation (189) that when such a beam of rays strikes a fixed crystal, the angle ϑ may be such that no reflection at all takes place. However, if we rotate the crystal slowly, each plane of its lattice will successively form all possible angles with the angle of incidence of the beam. These angles naturally always include angles (Fig. 103) at which the necessary reflection condition [Equation (189)] will be observed.
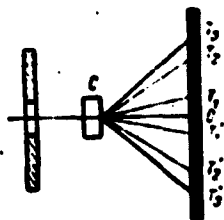
Fig. 102. Diagram of fixed-crystal method.

It is necessary to have available a single crystal of the material to be investigated in order to obtain x-ray patterns by the fixed-crystal and rotating-crystal methods. In running reactions in solid mixtures, however, we are obliged to deal with conglomerates or growths consisting of a large number of fine crystals in disordered orientation to one another. Their x-ray diffraction patterns are obtained by the so-called powder method, the principle of which reduces to the follow-
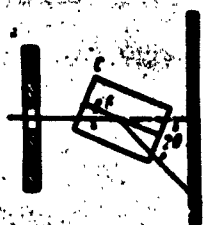
Fig. 103. Dia-
gram of rotat-
ing-crystal
method.
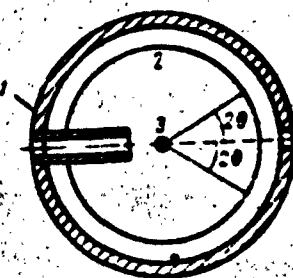
Fig. 104. Diagram of
powder method. 1)
chamber walls; 2)
photographic film;
3) powder.

ing. A cake or powder consisting of many crystals is placed between

a source of monochromatic x-radiation and a photographic plate. On the

plate, we obtain a series of concentric circles, each of which is the

result of reflection of the rays from a certain definite system of

parallel planes (e.g., the planes of a cube, octahedron, or other

figure) present in each of the crystals of the powder or cake.

In work by this method, the substance to be studied is rubbed to

a fine powder that will pass without residue through a screen having

10,000 or 16,000 holes per 1 cm^2, and placed in the center of a

cylindrical chamber in the form of a column 0.5-2 mm in diameter; the

photographic film is applied to the inside surface of the chamber (Fig.

104).
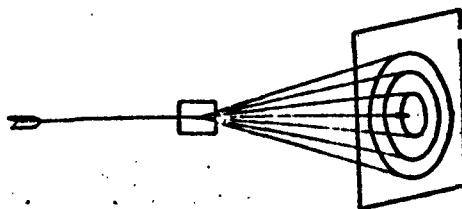
Fig. 105. Cones formed by re-
flected x-rays (powder method).

An x-ray that has passed through the narrow slit into the cham-

ber strikes one of the planes of the crystal at an angle θ and is re-

flected in a certain direction. This ray forms an angle ϑ with a number of other planes as well. As a result, a cone of reflected rays forms with its axis coincident with the primary ray.

Since the same reflection takes place at angles of 2ϑ, 4ϑ, and so forth, th $\imath$ satisfy Equation (189), we obtain a series of cones whose common axis is the direction of the primary ray (Fig. 105). Their track on a flat plate forms a series of concentric rings (Fig. 106), and when the film is bent into the shape of a cylinder, a series of lines where the cones intersect the cylinder (Fig. 107).

The position of the lines on an x-ray diffraction pattern depends on the distance $\underline{d}$ between the planes of the crystal. If the radius of the film is $\underline{r}$ and the distance from a given line of the x-ray pattern to the center of its central spot is $\underline{l}$, then

$$\frac{2\vartheta}{360} = \frac{l}{2\pi r};$$

from which

$$\vartheta = \frac{90l}{\pi r}.$$

(190)

Substituting the value of sin ϑ in Equation (189), we may easily determine the lattice parameter $\underline{d}$.
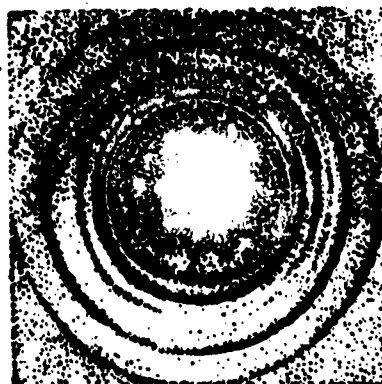
Fig. 106. X-ray diffraction pattern of copper powder, recorded on flat plate.

As for the relative intensity of the lines, this is determined primarily by the positioning of the atoms in the elementary cell of the lattice.

As a result of the above, each substance has its own peculiar configuration of the positioning and relative intensities of the lines on its x-ray pattern. Thus, the x-ray diagram may be regarded as an "x-ray identification card" that repre-

Fig. 107. X-ray diffraction pattern of carbide
deposit in high-speed steel, recorded on film.

sents a unique definition of the crystalline compound.

The x-ray identification patterns of several thousand substances
are known at the present time.

Comparison of the x-ray patterns of a specimen being investigated
and standard substances enables us primarily to establish their
presence in this object. Comparison of the intensities of the most
characteristic lines of the object and standard enable us to deter-
mine quantitatively the content of the given material in the object
(the ratio of these intensities is proportional to the content of the
corresponding substance in the object).

The data from x-ray analysis may be used to determine the dimen-
sions of the crystals composing the materials being investigated.
This is highly important for many branches of technology.

The possibility of determining the dimensions of structural ele-
ments (atoms, ions) of a crystal lattice with the aid of x-ray analy-
sis is of particular interest.

The atomic radii of metals may be determined directly from x-ray
analytical data by halving the experimentally established interatomic
distance. Thus, the shortest distance between the atoms in the struc-
tures of copper and magnesium is 2.55 and 3.2 A, respectively, from
which we have the radius of the copper atom as 1.27 and that of the
magnesium atom as 1.6 A. As concerns the dimensions of the various
elements in an ionic lattice, it is impossible to determine these in
the general case from x-ray analysis, since the distance d between
adjacent planes is equal to the sum of their radii in the case of con-

tact between an anion and a cation.

However, the distances between the planes of a crystal consisting of extremely small cations and large anions are determined by the sizes of the latter: in this case, the anions are in contact with one another, while the cations are situated in the vacant spaces between them. Thus, the interatomic distances Mg-Se = 2.73 and Mn-Se = 2.73 are the same, even though the manganese ion is larger than the magnesium ion. We may compute from this the radius of the anion [the radius of the divalent selenium ion is $(2.73 \sqrt{2})/2 = 1.92$]. However, knowing the radius of any one ion, we may use the values of the interplane distances $\underline{d}$ in various lattices containing this ion to compute the radii of other ions.

This circumstance was exploited at one time by Gol'dshmidt [9], who determined the radii of many ions on the basis of values for the radii of F = 1.33 A and O^{2-} = 1.32 A, which had been obtained by Vazashern on the basis of refractometric data.

X-ray structural analysis is one of the most highly perfected methods for the study of transformations that are accompanied by crystal-lattice changes. As a consequence, it is particularly helpful in investigation of polymorphic-transformation processes, processes in which chemical compounds form and in which solid solutions appear and decay.

The importance of the x-ray methods for study of reactions in mixtures of solids is difficult to overstate.

New and extensive possibilities for research into these reactions have been opened as a result of the development and mastery of x-ray apparatus that enables us to conduct and record observations at high temperatures [424-426]. This is important primarily because when a substance cools prior to recording of an x-ray pattern, changes in

its structure are possible.

The use of ionization methods for registering x-ray emission enables us to reduce the exposure by a factor of several hundred as compared with the conventional photographic method — another extremely important point.

The apparatus for ionization x-ray investigation of processes taking place at high temperatures (which is represented schematically in Fig. 108), consists of an x-ray source (x-ray tube), a goniometer, a high-temperature furnace, an x-ray receiver (gas amplifier), an electrometric direct-current amplifier and a recording device. Using such an apparatus to investigate the high-temperature processes related to the formation of cement clinker, Toropov, Konovalov et al. [427, 428] discovered a number of new facts and demonstrated the high effectiveness of the apparatus as applied to processes of this type.
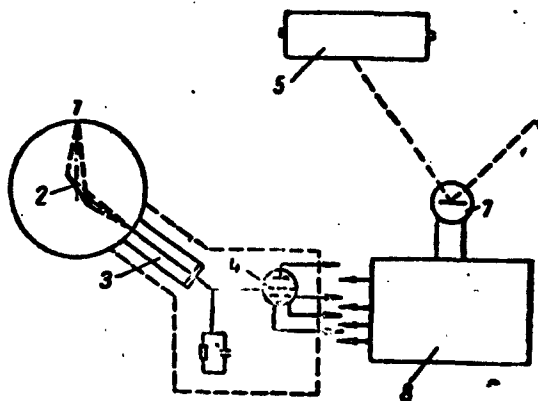
Fig. 108. Apparatus for x-ray ionization study of matter at high temperatures. 1) Source of x-rays; 2) ground specimen or rod; 3) receiver; 4) electron tube; 5) photographic drum; 6) lamp; 7) galvanometer; 8) power unit.

§5. ELECTRON-MICROSCOPE INVESTIGATION

Due to its wave nature, a flux of electrons that is intercepted by a diffraction lattice or some other obstacle is subject to diffrac-

tion just like a beam of light.

Here, Equation (189), in which wavelength is inversely proportional to the mass and velocity of the electrons and is determined by the equation

$$\lambda \simeq \sqrt{\frac{150}{V}} \text{Å}, \qquad (191)$$

where V is the voltage of the accelerating field in volts, remains valid.

At electron velocities corresponding to the field voltages customarily used in apparatus for electron-microscopic study (10^2-10^5 volts), wavelengths λ = 1 to 0.04 A correspond to the wavelengths of the most frequently used x-rays. As a result, the diffraction pattern obtained as a result of reflection of the beam of electrons by a crystal is quite analogous to the pattern obtained when x-rays are diffracted.

Fig. 109. Diagram showing formation of image of object of study in magnetic (a) and electrostatic (b) electron microscopes.

This opens broad possibilities for investigation of crystalline materials with the aid of the electron microscope.

Since the waves of electron beams are many times shorter than light waves, the magnifications attainable in this instrument considerably exceed those obtained in an ordinary optical microscope.

At the present time, electron microscopes exist that are capable of producing 200,000-fold magnifications and forming images of objects 25-30 A across.

The so-called electron gun, in which a thin tungsten wire is heated in a high-voltage field (50-100 kv) in a vacuum of the order of

10^{-4}-10^{-5} mm of mercury, serves as the source of electrons.

The electron flux passes through a narrow diaphragm, after which it is projected onto the object C (Fig. 109) by a condensing electro-magnetic or electrostatic lens 1. On emerging from the object C, the electron rays pass through the objective and projecting electromagnetic or electrostatic lenses 2 and 3, which function to produce an electron image of the object being examined. A screen that becomes fluorescent when bombarded by electrons or a photographic plate is placed in the plane of this final image.

The electron-diffraction pattern is obtained here by the use of simple accessories. Measurement of the distances between the rings and their relative intensities on the electron diagram (which, in general, has much the same appearance as the powder diagram) enables us to obtain exact identification of the substances examined.

The diffraction of an electron beam may also be used even without an electron microscope to obtain the electron pattern of a substance, which characterizes the most important properties of its structure.

This technique possesses certain essential advantages over the x-ray diffraction method. With considerably less powerful apparatus and much shorter exposure times, which are reckoned in seconds and fractions of a second, the electron diagram may show sharper lines than the x-ray pattern. This is accounted for by the more intensive effect of the electron beams on photographic emulsion as compared with x-rays and the possibility of more perfect monochromatization of the beam.

Certain specific properties of the electron beam limit the range of its application. The fact is that it is subject to considerably more intense scattering and absorption than a beam of x-rays. The probability of elastic collision between an electron and an atom is

10^7 times higher than the corresponding probability for x-rays. Thus, getting a distinct electron-beam diffraction pattern requires only a few surface layers of a crystal, while x-rays require tens and even hundreds of layers for the same objective.

As a result of the intensive scattering and absorption of the electron beam by the first layers of matter, these beams are capable of penetrating into the material only to a very small depth: where an x-ray passes to a depth of $1 \cdot 10^{-3}$ mm, an electron beam is capable of penetrating only to $1 \cdot 10^{-6}$ mm.

As a result, electron beams are used only for the investigation of surfaces, thin (e.g., oxide) films and crystalline substances that form thin platelets.

§6. IMMERSION METHOD

The simplest and quickest method of phase analysis, and one that has long been used in study of so-called solid-phase processes is the immersion method for determining the optical constants of crystals. It enables us to distinguish not only between materials of differing chemical composition, but also between different modifications of the same substance. The use of this method is not limited by complexity in the composition of the object being investigated and is frequently found very helpful in cases where it is difficult to get an unequivocal answer by chemical analysis.

The essence of the immersion method consists in microscopic observation of the powdered substance on its immersion into various liquids with known refractive indices that are easily checked with the aid of refractometers.

If the refractive indices of the material studied and the liquid are equal, the boundary between them is invisible. Otherwise, the appearance and displacement (toward the medium with the higher refrac-

- 375 -

tive index) of a bright band (the so-called Becke bands) when the microscope tube is raised serves as a basis for judging whether the object of investigation has a larger or smaller refractive index as compared with the liquid in which it is immersed.

Selecting two liquids whose optical properties differ very slightly from one another, with the refractive index N_1 of one somewhat larger and the index N_2 of the other somewhat smaller than the refractive index N_v of the material examined, we may assume with a certain degree of accuracy that

$$N_\text{в} = \frac{N_1 + N_2}{2}.$$

Obviously, a single determination of the disappearance boundary will be sufficient to find the refractive index of isotropic substances. Birefringent crystals require two different devices for the principal indices of refraction, which correspond to "extinctions" of the preparation between crossed Nicol prisms. In this case, a polarization microscope is employed.

The procedure of the immersion method is described in the special papers of Belyankin [429], Bokiy [430] and other authors. Here, it is only necessary to stress the great importance of immersion study of crystals in converging polarized light, which permits easy determination of their optical nature.

Improvements to the immersion method that have recently been introduced into laboratory practice (monochromatic light filters, temperature control and, accordingly, control of the standard-liquid refractive index during the observations) have simplified this method considerably and improved its accuracy.

§7. ISOTOPE METHOD

Modern solid-state chemistry takes advantage of the isotopy of elements with great effectiveness for various types of research.

We are indebted to Kheveshi [75] for introduction of the radioactive-isotope method for study of the processes that take place in solids. Using radium D and thorium B as radioactive isotopes of lead, Kheveshi applied this method in an investigation of self-diffusion in metallic lead and its halides. Subsequently, the radioactive-indicator method or, to use another term, the tagged-atom method, has undergone extensive development with the synthetic preparation of radioactive isotopes of almost all the elements. At the present time, it is being used successfully for study of the mechanism and kinetics of chemical reactions, corrosion of metals, adsorption and catalysis, as well as for investigation of friction, mechanical wear, and many other processes in a wide variety of disciplines.

"This new path of chemical research," remarked Brodskiy [431] correctly in 1951, "is one of the most important and promising in contemporary science. Extremely important results have been obtained with it in a very short time. It can be predicted with confidence that further progress in chemistry and kindred sciences will in the future be intimately related to the development and widespread application of the tagged-atom methods."

These methods are based on two singular properties of radioactive atoms: a) prior to their decay, their chemical behavior shows virtually no differences from the behavior of their nonradioactive isotopes and b) on decaying, the radioactive atoms emit energy that can be observed with comparative ease.

This energy may be used as a basis for determining extremely small quantities of a radioactive substance (for example, 10^{-16} of radioactive iodine — I^{131}). Thus, these methods are characterized by exceptionally high sensitivity.

The essence of the isotope method in its application to the study

of diffusion in solids reduces to the following. A thin layer of radioactive material is applied to the surface of the body to be investigated. Then the rate of penetration of the radioactive atoms into the solid is measured by determining the radioactivity at various depths in it at various intervals of elapsed time.

Here it is frequently possible to limit the activity determinations as follows: a) at various intervals of time at a given depth or b) at various depths at a given point in time.

Various methods and apparatus are employed to measure the radioactivity or, more precisely, a quantity that is proportional to it and thereby characterizes it (it is quite difficult to measure the true activity of a preparation). In practical work with tagged atoms, the most widely used techniques are the various variants of the ionization method, which is based on the ionization of molecules in a gaseous medium that is triggered by radioactive radiation.
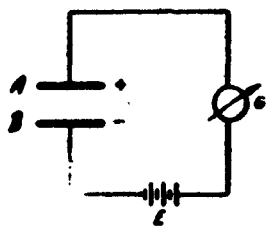
Fig. 110. Diagram
of ionization
method for measure-
ment of radioactiv-
ity.
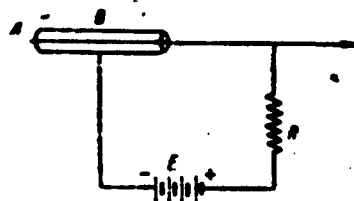
Fig. 111. Diagram of
Geiger-Mueller counter.
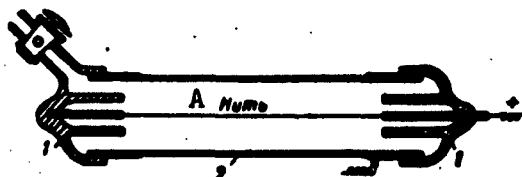
Fig. 112. Counter tube. 1) Glass;
2) metallic case. A) Filament.

The principle of this method is clear from Fig. 110. The electrodes A and B, which are connected to a current source E, are situated in dry air, which does not conduct current. Consequently, the circuit is open and the needle of the galvanometer G is on zero. When the air is ionized by radiation passing through it, a current which is indicated by the galvanometer and depends on the activity of the radiation will flow in the circuit.

Ionization chambers, Geiger-Mueller counters and counter tubes, which are described in detail in the specialized literature [432, 433], are based on this principle.

A schematic diagram of a cylindrical Geiger-Mueller counter is shown in Fig. 111. The metallic filament A, which is connected to the positive terminal of the current source E, is located in the metal cylinder B, which, as indicated on the diagram, is negatively charged. The ionization of the gas molecules in the cylinder B as a result of radiation gives rise to a strong current pulse. After minor amplification, this pulse may be registered or transmitted to a relay which operates a mechanical counter.

One typical variant of the counter tube, of which we make extensive use, is shown in Fig. 112.

Normally, only part of the radiation strikes the counter. It is necessary to take particular account of this fact in measuring the activities of solids. This is because the radiation losses and the resulting errors of determination in these cases depend not only on the design of the counter and the absorption of part of the radiation by its walls, but also on partial absorption of the rays by the preparation layer and, consequently, on its thickness, position and other such experimental conditions. To obtain reproducible results, therefore, it is necessary either to maintain strictly a definite thickness

and position of the preparations investigated or to dissolve thin layers of them before determining the activity.

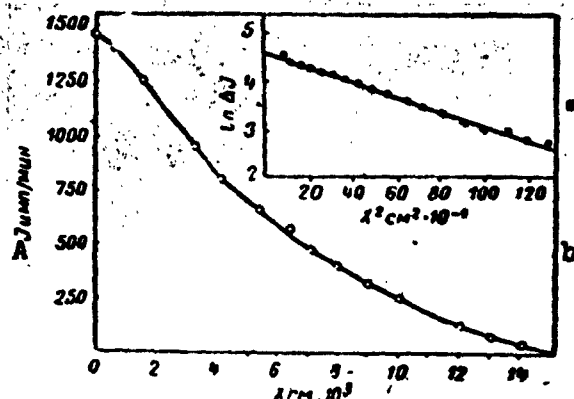Given these conditions, the relative error of the determinations normally does not exceed 20%.

Fig. 113. Self-diffusion of γ-iron. a) I = f(x); b) ln ΔI = f(x^2). A) Pulses per minute.
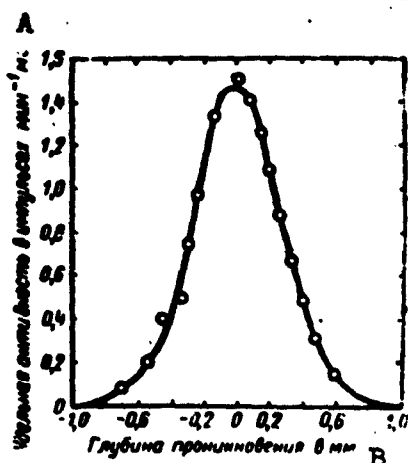

Fig. 114. Self-diffusion in silver: activity distribution after diffusion for ~10 days at 802°. D = = 3.97·10^{-10} cm^2·sec^{-1}. A) Specific activity in pulses per minute per mg; B) depth of penetration in mm.

The activity of the layer removed (without converting it to solution) may be determined by measuring the integral activity of the specimen.

Since the specific activity i of a thin layer at depth x is proportional to the concentration of diffused atoms in it, the diffusion equation may be written in the form

$$i(x, \tau) = \frac{i_0 a}{\sqrt{\pi D \tau}} e^{-\frac{x^2}{4D\tau}},\qquad (192)$$

where τ is the diffusion time, i_0 is the initial specific activity of the applied radioactive-isotope layer, a is the thickness of this layer and D is the coefficient of diffusion.
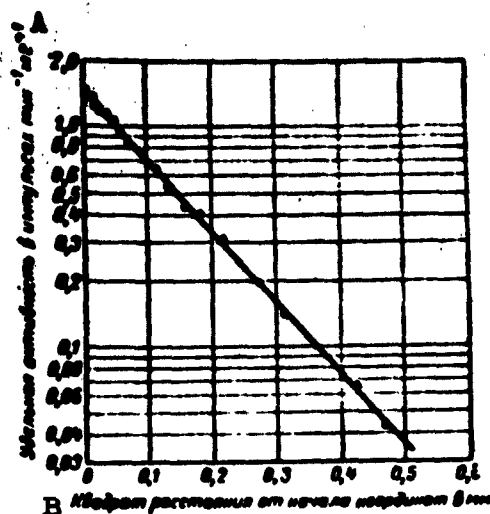
- 380 -

Fig. 115. Self-diffusion in silver: o, •) points of left and right segments of curve of Fig. 114, respectively. A) Specific activity in pulses per minute per mg; B) square of distance from co-ordinate origin in mm.

Assuming that the specific activity of the nth layer, $i_n(x, \tau)$, is equal to the difference between the integral activities of the specimen before and after removal of the layer (I_n, I_{n+1}), we obtain

$$\ln \Delta I = \ln (I_a - I_{a+1})$$

$$= -\frac{x^2}{4D\tau} + \ln \frac{L\sigma}{\sqrt{\pi D\tau}}. \qquad (193)$$

from which

$$D = -\frac{1}{4\tau \cdot \mathrm{tg}\,\alpha}. \qquad (194)$$

where α is the inclination of the line to the x^2-axis as given by Equation (193).

A diagram of $\underline{\ln}\ \Delta I = f(x)$ may be constructed by graphic differentiation of the experimental curve of I versus $\underline{x}$ (Fig. 113).

On the whole, however, the results obtained may, in accordance with the objectives of the study, be represented in various coordinates: specific activity versus distance from tagged surface of body (Fig. 114), specific activity versus square of distance from this surface (Fig. 115), diffusion coefficient versus the reciprocal of absolute temperature (Fig. 116) and other combinations.

The diagram of Fig. 114 uses the coordinates activity versus

Fig. 116. Self-diffusion coefficients of γ-iron as a function of T^{-1} [110]. A) log D, cm^2/sec; B) $1/T_{abs} \cdot 10^4$.

distance to represent self-diffusion data on radioactive silver, a thin layer of which was placed between two layers of nonactive silver [434, 435].

In the coordinates activity versus square of distance, the same experimental points lie on a straight line in accordance with Equation (193).

[Footnotes]

359   See, for example, V.V. Boldyrev, Metody izucheniya kinetiki
termicheskogo razlozheniya tverdykh veshchestv [Methods
for the Study of the Kinetics of Thermal Decomposition of
Solids], Izd. Tomskogo universiteta [Publishing House of
Tomsk University], Tomsk, 1958; Eksperimental'naya
tekhnike i metodam vysokotemperaturn. issledovaniy [Experi-
mental Technique and Research Methods for High Temperatures],
Tr. soveshch. po eksper. teknike i metody issledovaniya pri
vysokikh temperaturakh [Transactions of Conference on Ex-
perimental Technique and Methods for High-Temperature Re-
search], Izd. AN SSSR [Publishing House of the Academy of
Sciences USSR], Moscow, 1959; I.E. Kempbell (editor), Tekh-
nika vysokikh temperatur [High-Temperature Techniques], IIL
[Foreign Literature Press], Moscow, 1959.

360   A detailed survey of studies that have been made on differ-
ential thermal analysis and its applications particularly
for study of reactions in crystalline mixtures was made by
C.B. Murphy, Analyt. Chemistry, p. 2, 867, 1958.

362   Essential improvements to the method and technique of ther-
mographic analysis have been achieved recently in the work
of Soviet investigators (see L.G. Berg and M.Sh. Yagfarov;
V.P. Ivanova and F.Ya. Bindul', Yu. V. Sementovskiy; N.L.
Dilaktorskiy and L.S. Arkhangel'skiy, Trudy 5-go sovesh-
chaniya po eksper. i tekhn. mineralogii i petrologii [Trans-
actions of the Fifth Conference on Experimental and Technical
Mineralogy and Petrography], Izd. AN SSSR, Moscow, 1958).

[Footnotes]

359   See, for example, V.V. Boldyrev, Metody izucheniya kinetiki termicheskogo razlozheniya tverdykh veshchestv [Methods for the Study of the Kinetics of Thermal Decomposition of Solids], Izd. Tomskogo universiteta [Publishing House of Tomsk University], Tomsk, 1958; Eksperimental'naya tekhnike i metodam vysokotemperaturn. issledovaniy [Experimental Technique and Research Methods for High Temperatures], Tr. soveshch. po eksper. teknike i metody issledovaniya pri vysokikh temperaturakh [Transactions of Conference on Experimental Technique and Methods for High-Temperature Research], Izd. AN SSSR [Publishing House of the Academy of Sciences USSR], Moscow, 1959; I.E. Kempbell (editor), Tekhnika vysokikh temperatur [High-Temperature Techniques], IIL [Foreign Literature Press], Moscow, 1959.

360   A detailed survey of studies that have been made on differential thermal analysis and its applications particularly for study of reactions in crystalline mixtures was made by C.B. Murphy, Analyt. Chemistry, p. 2, 867, 1958.

362   Essential improvements to the method and technique of thermographic analysis have been achieved recently in the work of Soviet investigators (see L.G. Berg and M.Sh. Yagfarov; V.P. Ivanova and F.Ya. Bindul', Yu. V. Sementovskiy; N.L. Dilaktorskiy and L.S. Arkhangel'skiy, Trudy 5-go soveshchaniya po eksper. i tekhn. mineralogii i petrologii [Transactions of the Fifth Conference on Experimental and Technical Mineralogy and Petrography], Izd. AN SSSR, Moscow, 1958).

Manu-
script
Page
No.

376   в = v = issleduyemoye veshchestvo = material examined

Chapter 9

RESULTS OF INVESTIGATION OF
THE MOST IMPORTANT REACTIONS IN SOLIDS

§1. SINGLE-COMPONENT SYSTEMS

Let us consider the properties of certain single-component systems that are of great importance for technical chemistry of solids. These systems include SiO_2, TiO_2, ZrO_2, Al_2O_3, Cr_2O_3, Fe_2O_3 and certain others.

Silicon Dioxide

Silicon dioxide is capable of existence in various crystalline modifications. Numerous investigations have been devoted to their study (see, for example, [403, 404, 436-442]), and a considerable number of these have been published only during the last 5-7 years. The contradictory nature of the results obtained in many of these investigations and the inadequate study that has been devoted to the properties of certain modifications of silica (and tridymite in particular) enable us to judge its polymorphic transformations only with limited thoroughness.

The basic (first-order) modifications are, as we noted earlier, quartz, tridymite and cristobalite. Each of these may exist in the form of different (for example, α, β) forms or subvarieties, which are normally known as second-order modifications.

The temperature ranges of existence of quartz, tridymite and cristobalite were first established by Fenner [436].

Quartz is stable at temperatures below 870°. When α-quartz,

which crystallizes in the hexagonal system, is cooled, it undergoes an enantiotropic transformation into the low-temperature β-quartz. The temperature of this transition is 573°.

At a temperature of about 900°, quartz is transformed into cristobalite. In the presence of a mineralizer, the process in which cristobalite becomes tridymite takes place simultaneously; the latter is stable in the temperature range from 870 to 1470° (according to certain sources [437], formation of cristobalite in the temperature region of stability of tridymite is also impossible without a mineralizer). Thus, the formation of cristobalite is an intermediate step in the reversible process of transformation of quartz into tridymite.

The existence of three forms of the latter has been reliably established; these are the α-, β-, and γ-forms, although the literature also contains references to fourth and fifth forms of tridymite [438], as well as the opinion that tridymite cannot be regarded at all as an independent modification of silica [439].

The transitions of tridymite from the γ- to the β- and from the β- to the α- forms are reversible. When tridymite is heated, the temperatures of these transformations are respectively 117 and 163° (according to [437] 113-117° and 158-163°), and on cooling they occur at 73-71° and 151-147° [437].

At a temperature of 1470°, tridymite is transformed into α-cristobalite, which goes over into β-cristobalite at 200-270°. The β → α-cristobalite transformation point depends on the grain size of the original quartz and the time for which it is held at high temperature.

With two hours of holding at 1200° and grain sizes of 7-10, 24-28, 104-125 and 180-280 μ, the transformation temperatures of cristobalite from the β- to the α-form are respectively 250.5, 235.8, 208.3 and 211.2° [437].

Cristobalite that has been produced at temperatures below 1450-1470° is metastable and isotropic, so that prior to the detailed researches of Belyankin, many authors took this variety of silica for quartz glass; above 1450-1470°, stable anisotropic (at normal temperature) cristobalite is formed [403].

Cristobalite melts at 1713°. The cooled melt forms an amorphous isotropic quartz glass. The latter, in addition to its optical isotropy, possesses a low thermal-expansion coefficient that varies little with temperature, high electrical resistance and good permeability for ultraviolet light. All of this renders quartz glass an extremely valuable material for engineering.

In accordance with what we have said above, the polymorphic transformations of silica may be represented by the following scheme:
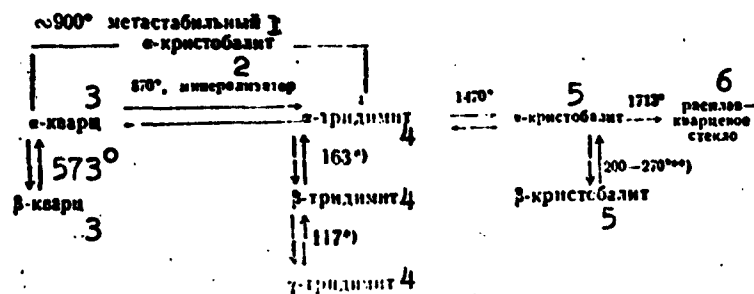
* On heating.
** Depends on grain size of original quartz.

1) Metastable α-cristobalite; 2) mineralizer;
3) quartz; 4) tridymite; 5) cristobalite; 6)
melt — quartz glass.

The structures of all the modifications of silicon dioxide encompassed by this scheme have not yet been studied in detail, although it is known that all of them are constructed from SiO_4 tetrahedra connected with one another in such a way that an oxygen atom is shared by two tetrahedra: this is the way in which the composition SiO_2 is formed. The differences between the structures of the various modifi-
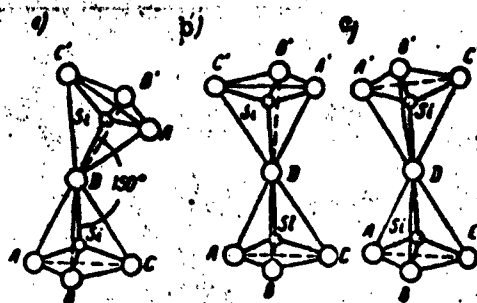
Fig. 117. Diagrams showing configuration of SiO_4 tetrahedra. a) In β-quartz; b) in cristobalite; c) in tridymite.

cations reduce to the differences in the relative positions of the SiO_4 tetrahedra in them. Naturally, the energy effect of the process in which silica goes from one modification to another, i.e., the work of rebuilding its lattice, depends on this difference.

This accounts for the primary formation of cristobalite from β-quartz. It follows from Fig. 117 that the transformation β-quartz → cristobalite requires only "straightening" of the SiO_4 tetrahedra, while the transition to tridymite requires further that they be rotated through $180°$ about the axis of symmetry. Transformations within the framework of a given modification of silica, such as $α \rightleftarrows β \rightleftarrows γ$-tridymite, involve only less significant changes in the way in which the SiO_4 tetrahedra are combined (chiefly, changes in angles). It is precisely for this reason that such transformations require the expenditure of small quantities of energy and take place readily at relatively low temperatures.

The properties of the various silica modifications differ greatly from one another (Table 38).

This applies in particular to the coefficients of thermal expansion of silica. When silica passes from one modification to another during heating, a stepwise change takes place in the volume of the specimen being tested. Thus, the β-quartz $\rightleftarrows$ α-quartz, α-quartz $\rightleftarrows$ α-tridymite and α-tridymite $\rightleftarrows$ α-cristobalite transformations are accompanied by volume changes of 2.4, 12.7 and 4.7%, respectively. On the basis of dilatometric study of silica, this last circumstance enables us to draw inferences as to the temperatures of its polymorphic

transformations and, to some degree, even concerning the extent of its transformation into the other modification under various conditions. The accuracy of determinations of this type, however, is highly relative, if only because the linear expansion of the specimen depends on the conditions of the experiment.

TABLE 38

Properties of Modifications of Silica

1 Модификация	2 Кристаллическая система	3 Удельный вес	Показатели светопреломления 4		5 Теплоемкость истинная в ккал/кг∙град	6 Температура области стабильности в град
			N_g	N_p		
β-кварц 7	Тригональная 11	2,65	1,553	1,544	0,286	573—870
α-кварц 7	Гексагональная 12	2,6	1,54	1,533	—	—
γ-тридимит	Ромбическая 13	2,31	1,173	1,469	—	—
β-тридимит 8	Гексагональная 12	2,29	—	—	—	—
α-тридимит		2,23	—	—	—	870—1470
β-кристобалит	Тетрагональная 14	2,32	1,487	1,484	—	—
α-кристобалит 9	Кубическая 15	2,21	1,466	—	0,3	1470 — 1713
Стекло кварцевое (расплав) 10	Аморфное 16	2,2	1,458	—	0,302	—

1) Modification; 2) crystalline system; 3) specific gravity; 4) refractive indices; 5) true heat capacity in kcal/kg-degree; 6) temperature region of stability in degrees; 7) quartz; 8) tridymite; 9) cristobalite; 10) quartz glass (melt); 11) trigonal; 12) hexagonal; 13) rhombic; 14) tetragonal; 15) cubic; 16) amorphous.

The melting points of the individual varieties of silicon dioxide show essential differences. Here, the following general rule is observed (page 154): The more stable phase has the higher melting point. The arrangement of the silica modifications in order of increasing melting point corresponds to this rule: quartz, tridymite, cristobalite.

The heating and cooling curves of silica enable us to fix the appearance of the heat effects that take place on its polymorphic transformations and hence to infer the temperatures of these transformations. Using modern research methods and precision instruments such as the vacuum adiabatic calorimeter [437], we may observe even
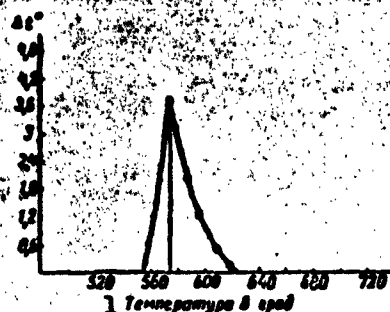
- 389 -

Fig. 118. Differential
heating curve of β-quartz
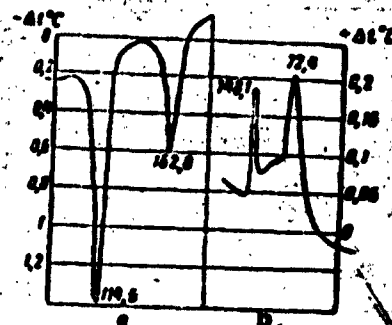(after Fenner). 1) Tem-
perature in degrees.

Fig. 119. Heating (a)
and cooling (b) curves
of tridymite [437].

very small changes in the test specimen during these processes.

Figures 118 and 119 show the breaks on the thermal-effect curves
at the transition points of quartz ($\beta \rightleftarrows \alpha$) and tridymite ($\gamma \rightleftarrows \beta$) and
($\beta \rightleftarrows \alpha$).

It has been established by isolation roasting of quartz grains
of different sizes that at temperatures of 1000-1400°, grains 2-5 μ in
size form for the most part cristobalite, while grains of sizes from
125 to 147 μ form tridymite preferentially.

It has become known [403, 404, 437-442] that small quantities
of certain mineralizers (such as calcium and magnesium oxides, titanium
dioxide, carbonates of lithium, sodium and potassium, and sodium
tungstate) vigorously promote the polymorphic transformations of
silica. The mechanism by which they act, which is undoubtedly related
to the appearance of a liquid phase in the system, has not yet been
finally established. On the other hand, it has been established [440]
that the polymorphic transformation of quartz is inhibited consider-
ably in the presence of even very small quantities (less than 1% on
the SiO_2) of aluminum oxide.

The polymorphism of silica may influence the kinetics of reac-

tions in crystalline mixtures containing this oxide (the so-called Khedval effect).

However, the practical importance of its transformations is associated chiefly with their enormous significance in the production and use of one of the most important refractory materials — Dinas.

Zirconium Dioxide

Zirconium dioxide is encountered in nature in the form of the mineral baddeleyite, which usually contains 80-90% and in some cases as much as 99% of ZrO_2. This and almost all other natural zirconium compounds (zircon, which is zirconium orthosilicate, and more complex zirconium silicates) normally contain a small quantity (from 0.1 to 4%) of an isomorphic hafnium dioxide impurity. It is extremely difficult to separate the latter from the ZrO_2* and its presence renders study of this oxide quite difficult (it is shown, for example, in the work of Berezhnoy and Karyakin [444] that many conclusions as to the polymorphic transformations of ZrO_2 have been inaccurate as a result of its polymorphism with HfO_2). Consequently, certain properties of ZrO_2 cannot be regarded as having been definitely established; this also applies to certain other zirconium compounds.

It has been established with certainty ([445, 446] and others) that ZrO_2 exists in two modifications: a monoclinic form that is stable at temperatures below $1000°$ and a denser pseudocubic (tetragonal) modification that forms at this temperature (according to some sources [447], at temperatures from $930-1040°$). The transition from the monoclinic modification to the tetragonal modification is accompanied by a decrease of approximately 7% in the volume of the ZrO_2 and is enantiotropic. According to Kon and Tol'ksdorf [448], tetragonal zirconium dioxide is transformed into cubic at $1900°$, and the latter undergoes an enantiotropic transformation into another

variety at 625°.

The scheme of all these transformations may be summarized as
follows:

$$\text{моноклинная} \underset{\xrightarrow{2}}{\overset{-1100°}{\rightleftarrows}} \text{тетрагональная} \overset{1100°}{\xrightarrow{\quad}} \text{кубическая I}$$
$$\downarrow 3 \uparrow$$
$$\text{кубическая II}$$

1) Monoclinic; 2) tetragonal; 3) cubic.

All these modifications of ZrO_2 possess a deformed CaF_2-type
lattice.

Monoclinic zirconium dioxide has a specific gravity of 5.7 g/cm^3,
a mineralogical-scale hardness of 6.5, and refraction as follows:
N_g = 2.2, N_m = 2.19, N_p = 2.13. The rather contradictory figures ob-
tained by various investigators for the melting point of ZrO_2 lie be-
tween 2585 and 2950°. The vapor pressure of this oxide at high tempera-
ture is very low: it amounts to ~6·10^{-1} mm at 2000° and ~16 mm Hg at
3000°, and its boiling point is 4300°.

Zirconium dioxide is used in engineering as a thermostable ma-
terial that resists mechanical damage and various types of chemical
attack at very high temperatures. As a result, the transition described
above from its monoclinic to its tetragonal modification is of great
practical significance: it takes place quickly, is accompanied by
shrinkage on heating and expansion on cooling, and causes deformation
of ZrO_2 articles.

References [444, 447, 449-453] and many others have been devoted
to study of this transition and ways to prevent it (stabilization of
the pseudocubic form of ZrO_2). The methods described in these papers
for stabilization of pseudocubic ZrO_2 are based on the formation of
this oxide with addition to it of the structurally similar oxides
CaO, MgO, V_2O_3, CeO_2 and other solid solutions of the cubic system
(CaF_2 type) that are stable over a wide temperature range. The acquisi-

tion of stable solid solutions is governed here by the relative simi-
larity between the cation radii of the oxides added and the radius of
the Zr^{4+} ion (0.82 A). As regards its chemical properties, ZrO_2 would
more likely be classified as an acidic than as a basic oxide. Even at
high temperatures, this oxide is practically inert with relation to
a very large number of substances. It does not react with fused metals,
silica, silicates or feldspar at temperatures below 2000°. Caustic
alkalis and acids (except for concentrated H_2SO_4 and HF) do not attack
it. It does not undergo chemical changes in an oxidizing atmosphere.
It is assumed [414] that partial transition of ZrO_2 into the lower zir-
conium oxides — Zr_2O_3 and ZrO — is possible in a reducing atmosphere,
but the existence and properties of these oxides have not yet been
established. The reaction of zirconium dioxide with carbon at tempera-
tures above 1900° results in the formation of zirconium carbide (but
only on the surface in the case of sintered ZrO_2).

Aluminum Oxide

Aluminum oxide is one of the most widely distributed oxides on
Earth. In nature, it is encountered in the form of the anhydrous
mineral corundum (α-alumina) and hydrated minerals (chiefly bauxite).
The precious stones ruby and sapphire represent varieties of corundum
that have been colored by trace impurities of oxides of chromium, iron
and titanium.

Pure corundum is encountered relatively rarely under natural con-
ditions. The tremendous demand of metallurgy and other branches of
technology for aluminum oxide of good purity are being satisfied at
the present time by its production from bauxites, nepheline and
other alumina-containing rocks by the so-called wet alkali, dry al-
kali (sintering) and other processes [454, 455].

Artificial corundum is produced on an industrial scale by electric

smelting of technical alumina or bauxite [456], as well as by melting chemically pure aluminum oxide in the oxyhydrogen-gas flame [457].

The properties of aluminum oxide are of great practical interest. As a result, many studies [167, 446, 458-462] have been devoted to study of, among other things, its transformations on heating. Certain of these results that touch upon polymorphic modifications of Al_2O_3 are contradictory and not sufficiently reliable. Data exist on the formation of five or even six modifications by aluminum oxide: α, β, γ, γ', δ, and ξ (the most important are characterized in Table 39).

However, the existence of only two independent modifications of alumina can be regarded as actually having been demonstrated; these are α- and $γ-Al_2O_3$. Modifications of AlO(OH) also correspond to these. $γ-Al_2O_3$, which crystallizes in the cubic system (a = 7.90 A) and has a specific gravity of 3.6 (according to other sources 3.42 and 3.47), is most simply prepared by roasting hydrargillite $Al(OH)_3$ or bemite, $γ-AlO(OH)$, to 700-900°. On heating to a temperature above 950-1200° (according to certain sources, above 750°), $γ-Al_2O_3$ undergoes a monotropic transformation into α-alumina with a 14.3% volume reduction. The α-modification of alumina is also obtained directly on heating of diaspore, α-AlO(OH).

$α-Al_2O_3$ (corundum) crystallizes in the hexagonal system and has a specific gravity of 3.99 (according to recent data of Murray et al. [416], the specific gravity of the $α-Al_2O_3$ single crystal is 3.96, although the specific-weight value given above for this modification should be regarded as more accurate). This modification of Al_2O_3 is stable at all temperatures. Figure 20 shows the structure of its lattice. This consists of two successive layers of oxygen ions, which form a hexagonal packing, with Al^{3+} ions positioned between the layers. The distance between two layers d = 2.16 A. The rhombohedral elementary

cell of the lattice is characterized by the values a = 5.12 A and
α = 55° 17' and contains two molecules of Al_2O_3. Figure 120 shows
the layer structure of spinel for comparison.

TABLE 39
Characterization of Polymorphic Modifications of
Alumina

1 Модификация	2 Система	3 Габитус	4 Удельн. вес в г/см³	5 Показатели светопреломления		6 Отношение к нагреванию
				N_o	N_e	
7 α-глинозем (корунд)	8 Гексаго-нальная	9 Таблицы и ромбоэдры	3,99	1,768	1,76	10 Плавится при 2050°
11 β-глинозем¹		12 Пластинки	3,3—3,4	1,68	1,65	13 При прокаливании до 1600° переходит в α-глинозем
14 γ-глинозем²	15 Кубическая	16 Октаэдры	3,6	1,736	—	Выше 1200° переходит в α-глинозем 17

1) The group of the so-called β-alumina includes
compounds of alumina with alkali and alkaline-
earth oxides, of the compositions: $Na_2O \cdot 11-12Al_2O_3$;
$K_2O \cdot 11-12Al_2O_3$; $CaO \cdot 6Al_2O_3$; $BaO \cdot 6Al_2O_3$; the con-
stants are given here for alkali β-alumina.
2) When precipitated alumina is roasted, it under-
goes transformation into $\gamma-Al_2O_3$ with a progres-
sive increase in refractive index and specific
gravity: N rises to 1.696 and d to 3.47. The con-
stants given in the table (1.736 and 3.6) for γ-
alumina apply to the distinctly crystalline
mineral obtained from the melt.

1) Modification; 2) system; 3) habit; 4) specific
gravity in g/cm³; 5) refractive indices; 6) rela-
tion to heating; 7) α-alumina (corundum); 8)
hexagonal; 9) tablets and rhombohedra; 10) melts
at 2050°; 11) β-alumina¹; 12) platelets; 13) be-
comes α-alumina on roasting to 1600°; 14) γ-
alumina²; 15) cubic; 16) octahedra; 17) undergoes
transformation to α-alumina above 1200°.

β-alumina, which, as noted by Belyankin [463], always forms in
electrosmelted and recrystallized corundum, is essentially an aluminate
(see note to Table 39) of the composition $RO \cdot 6Al_2O_3$ or $R_2O \cdot 11-12 Al_2O_3$.
Its formation is due to the content of alkali-metal (Na_2O to 0.5%) and
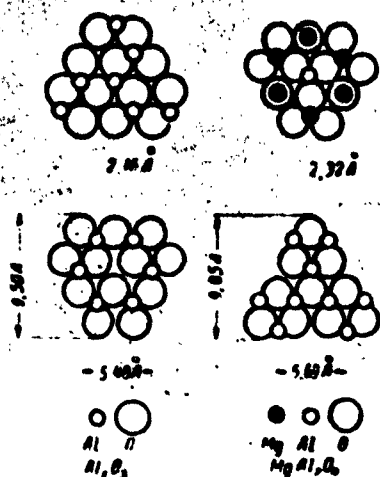alkaline-earth oxides as impurities in technical alumina.

Fig. 120. Structure of layers in lattices of corundum and spinel.

The properties of the various forms of alkaline β-alumina have been investigated in detail by Toropov et al. [460-462].

The γ'-modification of Al_2O_3, which forms at the electrodes in electrolysis of aluminum oxide, has been the subject of very little study. It has a crystal lattice that differs very slightly (simply by the presence of vacancies) from the γ-Al_2O_3 lattice (Vervey, 1935) and is quite probably only the γ-modification with a defect crystal structure.

In much the same way, δ-Al_2O_3, which has been identified by x-ray analysis and is produced on gentle roasting of $AlCl_3 \cdot 6H_2O$, may be regarded as a degraded α-form of aluminum oxide: on heating of δ-Al_2O_3,

TABLE 40

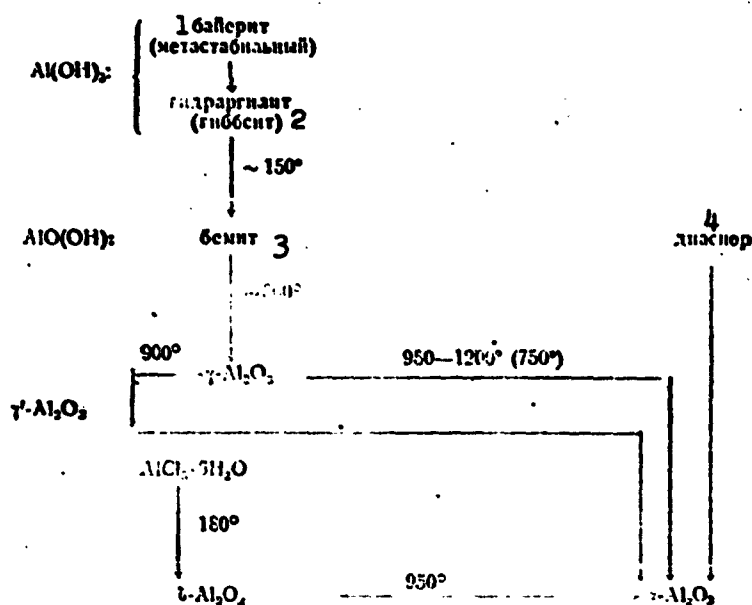Change in Specific Gravity of δ-Al_2O_3 on Heating (for 15 days)

1 Температура в град.	2 Удельный вес	
	3 по рентгеновским данным	4 по непосредственному определению
250	2.38	2.4
450	2.45	2.52
700	3.45	—
850	3.58	3.6
960	3.66	3.65
1200	3.9	—

1) Temperature in degrees; 2) specific gravity;
3) by x-ray analysis; 4) by direct determination.

its specific gravity gradually increases (Table 40), and at 1200° the structure is perfectly identical with that of α-Al_2O_3 (corundum);

here, the total volume reduction is about 40%.

It has not been possible to establish exactly the region of ex-
istence of yet another form of aluminum oxide, namely, the cubic ξ-
form noted by Ryshkevich [446]. As regards structure, however, ξ-Al_2O_3
is perfectly identical to the α-modification [458, 459].

The transformations of alumina and its hydrates on heating may be
represented by the following scheme:

1) Bayerite (metastable); 2) hydrargillite
(gibbsite); 3) bemite; 4) diaspore.

The physical properties of the most common and most extensively
studied α-modifications of alumina and their variation with tempera-
ture are described in detail in the literature [167, 413, 446, 454,
455 and others]. It is important to note in connection with the phe-
nomena of interest to us only that although the maximum temperature
at which α-Al_2O_3 is used as a refractory material is generally taken
as 1950°, its deformation under load may intervene at 1860-1900° [446,
464], and at an even lower temperature in tne presence of impurities.

The vapor pressures of α-aluminum oxide at temperatures of 2360,

2410, 2490, 2547 and 2580° are, respectively, 6, 18, 22, 50 and 55 mm Hg, while the boiling point computed from these data is 2980 ± 60° [446].

Chromic and Ferric Oxides

On the basis of its crystal structure, chromic oxide, which is widely employed in practice under various names, would be classified in the trigonal subclass of the hexagonal system. The elementary lattice cell of this oxide contains two molecules and has the parameter 5.35 A. The color of Cr_2O_3 varies from greenish (in a fine powder) to almost black (in large crystals). Its density is 5.22, its hardness approaches that of corundum, and its melting point is 2435°. Cr_2O_3 is a semiconductor and possesses paramagnetic properties.

According to certain investigators, chromic oxide may exist in two modifications: γ- and α-Cr_2O_3, of which the former, low-temperature form undergoes monotropic transformation to the latter when heated above 800°. However, the magnitude of the volume effect and a number of other characteristics of this transition are not exactly known.

Cr_2O_3 forms chromites with many oxides of other metals (see §2 of Chapter 9); some of these chromites are of great importance for the technology of refractory materials.

More detailed information on the physical and chemical properties of chromic oxide is available to the reader in Edi's monograph.*

Ferric oxide is known in the form of three modifications: α-, γ- and δ-Fe_2O_3; the first two are of great practical importance. The hexagonal form of δ-Fe_2O_3 forms on oxidation of alkaline solutions of ferro salts and undergoes monotropic transformation to α-Fe_2O_3 at a temperature of 110°.

The metastable γ-modification can be prepared by low-temperature oxidation of magnetic iron oxide. Thus, like Fe_3O_4, γ-Fe_2O_3 crystal-

- 398 -

lizes in a cubic lattice of the spinel type (a = 8.32 A) and has ferromagnetic properties. The difference between the lattices of Fe_3O_4 and γ-Fe_2O_3 reduces to the fact that all points are occupied in the first, while in the second, certain of the iron points are vacant. Between γ-Fe_2O_3 and Fe_3O_4 there is a whole continuous series of substances having intermediate compositions; these may be regarded as solid solutions of γ-Fe_2O_3 and Fe_3O_4. In the Fe-O system, however, only a limited region of solid solutions is realized out of this continuous series as a stable phase; this develops considerably only at high temperatures.

According to available data, Fe_2O_3 possesses a certain solubility in Fe_3O_4 (its range can be indicated only approximately); on the other hand, the magnetic oxide is insoluble in Fe_2O_3.

At a temperature of 817°, γ-Fe_2O_3 undergoes monotropic transformation into the α-form with a volume reduction of .5%.

α-Fe_2O_3 possesses the rhombohedral structure of corundum and is the stable form of ferric oxide. Attempts to determine the melting point of this oxide encounter difficulties related to its high dissociation vapor pressure, which results in formation of a melt composition intermediate between Fe_2O_3 and Fe_3O_4 (but nearer to the latter). Consequently, literature data on the melting point of Fe_2O_3 must be approached with great caution; it appears that this temperature is much higher than 1600° for the pure oxide.

According to the most complete and apparently most exact data of Greyg [465], the dissociation vapor pressures of Fe_2O_3 at temperatures of 1100, 1300, 1400, 1500 and 1600° are, respectively, $2.6\cdot10^{-5}$, $19.7\cdot10^{-3}$, 0.28, 3 and 25 atmospheres.

According to Gel'd, Yesin et al.,* the dissociation-vapor-pressure curve of Fe_2O_3 has discontinuities at temperatures of 830 and 900° that

are related to the phase transformations of this oxide. There are also references to transformations of ferric oxide at temperatures below 0°, but very little study has been devoted to them.

§2. SPINELIDES AND SIMILAR COMPOUNDS

Compounds of the general formula MeR_2O_4, which crystallize in the isometric system, are usually known as spinelides.

Here, Me and R are, respectively, di- and trivalent cations; in the above sense, therefore, a spinelide is a compound of two oxides: $Me^{++}O$ and $R_2^{+++}O_3$.

Cu, Be, Mg, Ca, Sr, Ba, Zn, Cd, Pb, Mn, Fe, Co and Ni most frequently figure as the divalent cations in these compounds. The trivalent cation is usually Al, Cr, Mn, or Fe. Ga, In, La, V, Sb and others are used more rarely.

The spinelides are characterized by a crystal lattice of the cubic system that was first studied in the so-called noble spinel $MgAl_2O_4$. This is a face-centered (probably atomic-ionic) lattice with eight molecules in the elementary cell.

However, not all compounds that would be classified as spinelides on the basis of their formulas (MeR_2O_4) crystallize in the cubic system. Thus, $BeAl_2O_4$ (crysoberyl) and $CaCr_2O_4$ have rhombic lattices and $SrAl_2O_4$ has a tetragonal lattice.

At the same time, a number of compounds of the type $Me_2^{2+}R_2^{4+}O_4$ or, otherwise written, $2Me^{++}O \cdot R^{++++}O_2$, such as Mg_2TiO_4, crystallize in the spinel lattice and may therefore be classified as spinelides (Co, Fe, Mg, Zn and other ions may figure in this group of compounds as the divalent cations and Ti and Sn as tetravalent cations).

As a result, it is expedient to classify compounds of both the types $MeO \cdot R_2O_3$ and $2MeO \cdot RO_2$ that crystallize in the isometric system as spinelides.

This is the principle to which we shall adhere below in distinguishing among the spinelides: a) the spinels proper, which have the formula $MeO \cdot R_2O_3$ and a cubic lattice and b) certain other compounds.

The spinelides have acquired great importance in technology. They are used with success in the production of abrasives, refractory materials, ceramic products, and mineral dyes. Certain spinelides are also of interest as catalysts [466].

The crystal structure and crystal-optical, physicomechanical, certain thermal, magnetic, electrical and other properties of many compounds in this group have now been studied. Certain of their properties, as, for example, color (when spinels are used as dyes), melting point (when they are used as refractory and high-refractory materials), conductivity (when they are used as electrically insulating materials) and certain others are of direct practical interest. Conductivity data may be used for indirect inferences as to the internal structure of the spinels and their solid solutions.

On the basis of conductivity, the pure spinels may be classified into three groups [467]: aluminates, which have very low conductivities (resistivity R at 900° of the order of 10^5 to 10^6 ohms-cm), chromites with medium conductivity (at 900°, R ~ 10^3 to 10^4 ohms-cm) and ferrites with rather high conductivity (R_{900} ~ 10 to 10^2 ohms-cm); magnetite Fe_3O_4 has a particularly high conductivity on a level with those of metals.

It should be noted that conductivity is determined in aluminates by the divalent cation, and in chromites and ferrites (with the exception of ferrous-oxide compounds) by the trivalent cations.

One of the most important properties of spinel systems is the ease with which substitutional solid solutions are formed between them; this is due to the similarity between the lattice parameters of

the various spinels. Thus, unlimited solubility of crystalline $MgAl_2O_4$ and $MgCr_2O_4$, $FeCr_2O_4$ and $FeFe_2O_4$, etc., has been established [468, 469]. It is thought that aluminates, which have a spinel lattice, also possess unlimited mutual solubility. Chromites and ferrites are easily miscible [470], and so forth.* Certain spinels form solid solutions with oxides of trivalent metals. Thus, $MgAl_2O_4$ forms such solutions with aluminum oxide, and particularly readily with its γ-modification, which has a crystal lattice closely similar to the spinel lattice.

As has been noted on many occasions in the literature [395, 414 and others], the ability to form solid solutions is of great importance in the manufacture and service of spinel refractories.

On the basis of Vegard's rule [73], which has been confirmed for a number of spinel systems by experiment [472], it is frequently assumed that the properties of spinel phases are determined by the properties of the last members of the series in question and their content in the mixture. Actually, this rule is of limited significance for the real systems (see §1 of Chapter 2).

A significant increase in the volume of the crystalline phases is observed in the synthesis of many spinels and in formation of their solid solutions. According to Lovel [473], who made a detailed study of this phenomenon in vanadium spinels and certain others, experiments with various isomorphic substances that form solid solutions on heating indicated that expansion on solid-solution formation is a property of spinels. There is as yet no rigorous theoretical basis for this phenomenon.

An important property of the spinelides is their ability to enter into substitution reactions (a large number of such reactions has now been studied). As a result, we may distinguish three types

1 Химическая формула	2 Минералогическое название	3 Кристаллографическая система	4 Параметр решетки в Å	5 Удельный вес	6 Твердость	7 Температура плавления, град	8 Характер проводимости
$MgAl_2O_4$	Шпинель (9)	Кубическая (13)	8,09	3,55	8	2135	Электронная (14)
$ZnAl_2O_4$	Ганит (10)	"	8,06	4,58	7,5—8	1900	
$CoAl_2O_4$	—	"	8,08	4,37	>7	1900	Дырочная (15)
$NiAl_2O_4$	(11) —	"	8,03	4,15	—	2020	
$MgCr_2O_4$	Магнезио-хромит	"	8,31	4,3	~6	2330	
$FeCr_2O_4$	Феррохромит (12)	"	8,34	5,11	—	2250	

1) Chemical formula; 2) mineralogical name; 3) crystallographic system; 4) lattice parameter in Å; 5) specific gravity in g/cm^3; 6) hardness; 7) melting point in degrees; 8) nature of conductivity; 9) spinel; 10) ganite; 11) magnesiochromite; 12) ferrochromite; 13) cubic; 14) electronic; 15) hole.

of reactions, e.g., of aluminate spinels with oxides [395]:

    1) aluminates and oxides form four phases, such as

$$MgO + BeAl_2O_4 \rightarrow MgAl_2O_4 + BeO;$$

    2) the aluminates and oxides form solid solutions, e.g.,

$$MgO + NiAl_2O_4 \rightarrow (Ni, Mg)O + (Mg, Ni)Al_2O_4;$$

    3) the aluminates exhibit full miscibility, while the oxides have incomplete miscibility, as, for example, in systems with zinc oxide.

A property of many spinelides that is of great technical value is their high refractoriness (see, for example, Table 41). This is a characteristic of the true spinels $MgAl_2O_4$, $ZnAl_2O_4$, $CoAl_2O_4$, $NiAl_2O_4$, $MgLa_2O_4$ ($t_{pl} = 2030^\circ$), $MgCr_2O_4$, $FeCr_2O_4$, and also of such compounds as $BeAl_2O_4$, $SrAl_2O_4$, $CaCr_2O_4$ and certain others.

Here, spinelides whose composition does not include easily reduced or oxidized cations are quite stable under heating in various gaseous media.

The properties of compounds of this group are described in

greater detail in References [395, 414, 446, 472, 473, 475-478] and many others.

Some spinelides, chiefly those of complex composition incorporating various di- and trivalent cations, are encountered in nature in the form of minerals; these include, for example, picotite (Mg, Fe)·(Al, Cr)$_2$O$_4$. Practically no large deposits of pure spinels (except for the chromites) are encountered.

There are, however, broad possibilities for producing them artificially on the basis of rich raw-material resources that exist both in the Soviet Union and in many other countries. In this connection, the artificial synthesis and industrial production of various spinelides are of great importance and have been worthy objects of numerous research studies.

Even Morozevich [479], working more than 60 years ago, studied the conditions of formation of a number of spinelides at high temperatures. In 1903-1905, Chirvinskiy [480] became the first to subject numerous data obtained on spinelide synthesis during the last century to critical analysis. In the present century, and particularly in the last 15-20 years, studies in this field have been developed extensively and researchers of many countries are prosecuting them.

Various methods exist for producing spinelides. Methods based on reactions in mixtures of crystalline solids at high temperatures have the greatest technical importance among these. All spinelides known at the present time can be produced with the aid of such reactions. If necessary, practically pure substances can be produced.

At the present time, many such reactions have been studied, the mechanism, kinetics and intensifying factors of many of them have been investigated on the examples furnished by a number of spinels, such as ZnO·Fe$_2$O$_3$ (page 157 et seq.), MgO·Al$_2$O$_3$ (page 180) and others,

- 404 -

the multistage, stepwise nature of the processes in which they form has been demonstrated, and methods for industrial production of many spinelides have been worked out.

Together with this, as will become clear from the exposition to follow, the various spinel systems and the various reactions used in producing the spinels have not been studied with the same degree of thoroughness. Some of the pertinent data offered by the various investigators are contradictory and some of the experimental data are compromised by incompleteness and inadequate precision. The number of possible spinels has not been exhausted by the compounds described in the literature; it is very large and as yet far from completely covered by synthesis. For example, spinelides that contain rare-earth oxides remain virtually unstudied. Thus, there is still much room for research in this field.

The preparation reactions of the spinelides will be considered in the separate systems below with the object of acquiring a certain degree of classification and for convenience in setting forth the material.

Systems With CuO

Copper spinelides are unknown in nature in their pure form, with the exception of crednerite $CuMn_2O_4$. They have been produced synthetically and studied in connection with various technical problems.

The formation temperature of these spinelides from the oxides is comparatively low, but their synthesis is made difficult by the low stability of cupric oxide: on heating, it is converted into cuprous oxide, and this results subsequently in formation of compounds of the type $Cu_2O \cdot Me_2O_3$.

The formation and properties of $CuAl_2O_4$ have been studied by Khedval [481, 482], Krauze [483] and other investigators. It has been

established that this reddish-brown compound crystallizes in the cubic system with a lattice parameter of 8.064 A. The temperature of its appreciable rate of formation is 900°. At this temperature, the yield of this spinelide in Krauze's experiments was 75% of theory after two hours. Excellent $CuAl_2O_4$ crystals were obtained in a potassium-chloride melt.

Since cupric oxide converts quite rapidly into Cu_2O at 1100° in an air atmosphere (by the reaction $4CuO \rightarrow 2Cu_2O + O_2$), the formation of $CuAl_2O_4$ is studied in a medium of pure oxygen at temperatures of 1100° and higher.

Cupric oxide reacts·more slowly with Cr_2O_3 than with aluminum oxide. The chemical reaction between CuO and Cr_2O_3 takes place at a marked rate at 920°. The product of this reaction, $CuCr_2O_4$ (according to certain sources, $Cu_2Cr_2O_4$), is a green compound of the cubic system with an elementary cube having a side of 8.34 A.

The formation of cupric-oxide ferrite, which was studied in detail by Mostovich and Uspenskiy [484], takes place at a noticeable rate at 600° and rapidly at 750°. This compound, which is brown in color and possesses high magnetic susceptibility, may exist in cubic and tetragonal modifications. When a mixture of ferric oxide and cupric oxide is heated to temperatures of $800-900^\circ$ and subsequently cooled sharply, a ferrite of the cubic modification is produced. Slow cooling of the reaction mixture results in formation of the tetragonal modification, which is stable at $350-400^\circ$ (cuprous-oxide ferrite, which forms at $t \geq 1100^\circ$, crystallizes in the hexagonal system).

Copper spinelides are of interest for metallurgy ($CuFe_2O_4$) and are also used as ceramic pigments ($CuFe_2O_4$, $CuCr_2O_4$) and catalysts ($CuCr_2O_4$).

Systems With BeO

Only one beryllium spinelide, crysoberyl ($BeAl_2O_4$), is known in nature; this is infrequently encountered in beryllium-bearing rocks. This compound can also be synthesized, for example, by reacting BeO and Al_2O_3 in crystalline mixtures.
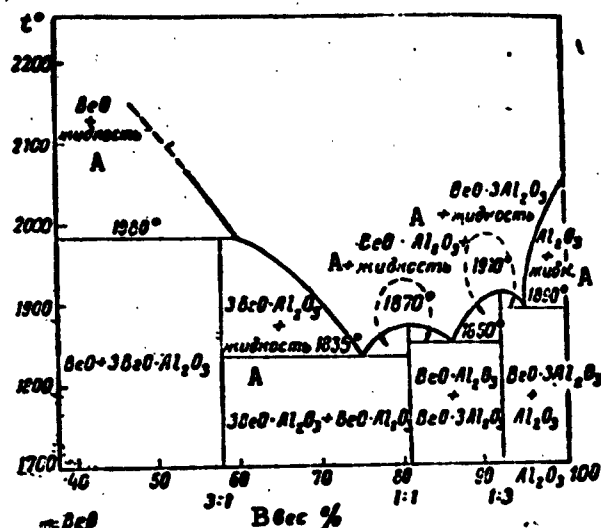

Fig. 121. Diagram of state of Al_2O_3-BeO system. A) Liquid; B) per cent by weight.

Until comparatively recently, only the single compound crysoberyl was known in the BeO-Al_2O_3 system.

However, new compounds belonging to this system were discovered and then subjected to detailed study in 1947 and 1956: BeO·$3Al_2O_3$ [485, 486] and $3BeO·Al_2O_3$ [487]. The properties of the former are described most thoroughly and accurately in the report by Budnikov et al. [485], while the second is described by Galakhov [487]. $3BeO·Al_2O_3$ possesses a mean refractive index N = 1.720 and melts at $1980°$ with decomposition into BeO and liquid.

Crysoberyl crystallizes in the orthorhombic system. Its melting point is usually taken as $1870°$ [413]. However, it has been established

by experiment that it decomposes into the oxides even before melting, at 1800°. In view of this, and as follows from the diagram of state of the Al_2O_3-BeO system (Fig. 121), the liquid phase may appear at temperatures below 1870° when crysoberyl is heated.

At high temperatures, the beryllium oxide in crysoberyl is easily replaced by stronger bases, e.g., by magnesium oxide:

$$BeO \cdot Al_2O_3 + MgO \rightarrow MgO \cdot Al_2O_3 + BeO.$$
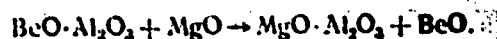
This reaction takes place readily on heating of crystalline powdered mixtures of $BeAl_2O_4$ with MgO.

$BeAl_2O_4$ is of a certain amount of interest in refractory ceramics. Crysoberyl in the form of brightly colored crystals is a semiprecious stone.

As yet, the technical importance of other beryllium spinelides is insignificant, but the processes in which they form have nevertheless been studied on a number of occasions.

The reaction of BeO + Cr_2O_3 in mixtures has been studied by various methods. As long ago as 1916, Mil'bauer observed a chemical reaction between these oxides under oxygen pressure at a temperature of 480°. The pigment sorption minimum in the BeO-Cr_2O_3 system occurs as low as 300°, and the maximum at 600°. The formation of the chemical compound $BeCr_2O_4$, the chromium analog of crysoberyl, has been established in the system; this has the orthorhombic crystal lattice of the latter with parameters similar to it [488]. A field of primary $BeCr_2O_4$ crystallization is noted in the ternary system with Cr_2O_3.

The property changes of BeO + Fe_2O_3 mixtures on heating has been the object of numerous research studies.

Forest'ye and Galan [489] obtained $BeFe_2O_4$ from solutions of $BeCl_2$ and $Fe(NO_3)_3$ by precipitation with ammonia and heating the resulting precipitate.

- 408 -

On the basis of magnetometric measurements, the authors established that at temperatures above 620°, beryllium ferrite decomposes into the oxides. In the opinion of the authors, this compound possesses the structure of lepidocrite (according to Gil'pert and Ville [490], $BeFe_2O_4$ has a structure of the hematite type).

In contradiction to this, Khyutting et al. [491, 492] and Yenkel' [493], proceeding from an investigation of the catalytic effect of $BeO + Fe_2O_3$ mixtures on the decomposition of N_2O and oxidation of CO, maintain that beryllium oxide does not react with ferric oxide.

The investigations of Forest'ye and Galan are more exact. However, in view of the above contradictions, the process in which $BeFe_2O_4$ forms should be subjected to further experimental investigation.

Systems With MgO

Among the magnesium spinelides, those encountered under natural conditions are $MgAl_2O_4$ (spinel) in the form of solid solutions with other minerals, $MgCr_2O_4$ in the form of solid solutions with $FeCr_2O_4$ (chromite), and $MgFe_2O_4$ (magnesioferrite). All of them, and many other spinelides of this group, have also been produced synthetically.

The synthesis and properties of $MgAl_2O_4$, "noble spinel," have been studied in greatest detail. It was synthesized by numerous mineralogists as long ago as the middle of the XIX Century. In 1847, Ebel'men produced $MgAl_2O_4$ from a mixture of the oxides in the presence of B_2O_3 as a process accelerator.

The synthesis of spinel was subsequently studied by a number of investigators using dilatometric and other methods, and the accelerating influence of small additives (~2%) of B_2O_3 and WO_3 was confirmed. However, Renkin and Mervin [474] synthesized $MgO \cdot Al_2O_3$ by fusing the pure oxides together.

Nikogosyan et al. [494-496] and Bazilevich [475] produced this

compound by sintering clay with magnesium oxide. These same authors were the first to devote detailed study to the properties of spinel as a refractory material. Bazilevich studied the synthesis of $MgAl_2O_4$ from chemically pure oxides of magnesium and aluminum, firing a briquetted mixture of them at 1300-1750° without the use of any additives. The product contained 86% spinel 2 hours after the start of the experiment at 1750°.

The process in which spinel forms in a mixture of crystalline reagents was subsequently studied under various conditions by numerous authors. Here, it was established, among other things, that the process takes place at a noticeable rate at temperatures as low as 1000° and even lower.

In 1937, Feodot'yev and Vogman [497] made a detailed study of the course of this reaction at 1200, 1300, 1400, 1500 and 1600°. Here, the starting materials were $Al(OH)_3$ and MgO.

Microscopic examination of the products obtained as a result of two hours of roasting a mixture of these substances in the absence of additives and in the presence of B_2O_3 and $FeCl_3$ led the authors to the conclusion that when magnesium oxide reacts with alumina the result is $\beta-Al_2O_3$ (Table 42). The authors related the formation of spinels and the influence of the accelerating additives to the temperature limit of existence of this compound.

The observations of Feodot'yev and Vogman are of interest for the production technology of refractory materials.

However, it has been established by other investigators, including later ones, that the primary product of the reaction between MgO and Al_2O_3 is spinel, even at temperatures lower than 1000°; $\beta-Al_2O_3$, on the other hand, is to be regarded in this case only as a side product of this reaction.

Khyutting et al. [491] established in an investigation of the process in which spinel is prepared in a mixture of MgO with γ-Al_2O_3 that the catalytic action of this mixture on the reaction forming CO_2 from CO and O_2 has a narrow but quite distinct region of high activity, the maximum of which corresponds to approximately $450°$. A sharp drop in this activity is observed at temperatures above $600°$. In the interval between 600 and $700°$, marked transformation of the reaction product into crystalline spinel begins.

In a detailed investigation of the process in which $MgAl_2O_4$ forms in a mixture of MgO with α-Al_2O_3, Yander and Pfister [498] state that the "coating" period in this process takes place at temperatures from 400 to $500°$ (Fig. 122); they found the hygroscopicity maximum for a reaction mixture roasted at $500°$. Heating the mixture to a temperature of $600°$ results in formation of disordered reaction shells that grow rapidly when the temperature is raised to $800°$. Beyond this point, the first spinel crystals begin to form, and this is accompanied by a sharp increase in the apparent heat of activation of the decomposition process of nitrous oxide passed over the crystalline mixture and the presence of a second maximum of its hygroscopicity. These first $MgAl_2O_4$ crystals possess large lattice defects. Yander detected spinel crystals in mixtures of MgO with Al_2O_3 at $920°$, using x-ray techniques. This is accompanied by a considerable drop in the catalytic activity of the reaction mixture, as is shown by the use of N_2O and CO + O_2 (curves 4 and 5) and in its adsorbing ability. According to Yander's observations, the defects in the structure of the spinel crystal lattice had vanished completely when the reaction mixture was heated to $1000°$.

The mechanism of spinel formation from the oxides is of great interest.

TABLE 42

Progress of Spinel Formation According to
Fedot'yev and Vogman [497]

1 Температура в град.	2 Фазы, найденные при микроскопическом исследовании продуктов обжига смесей		
	Al(OH)₃ + MgO	To же, с добавкой 2% B₂O₃ 3	To же, с добавкой 2% FeCl₃ 4
1200	5 β-Al₂O₃; MgO	β-Al₂O₃; α-Al₂O₃·MgO шпинель (около 10%)	6 Значительное количество β-Al₂O₃, MgO шпинели очень мало
1300	7 β-Al₂O₃; MgO; появляется α-Al₂O₃ и шпинель (10—15%)	8 β-Al₂O₃ перешел в α-модификацию; шпинели 30—40%	9 Те же фазы; шпинели мало (около 40%)
1400	10 Те же фазы; шпинели 15—20%	11 Те же фазы; шпинели около 90%	12 Количество шпинели возросло
1500	13 β-Al₂O₃ очень мало; шпинели 50—60%	—	14 β-Al₂O₃ нет; присутствуют α-Al₂O₃ очень мало и шпинель (85—90%)
1600	β-Al₂O₃ нет; полное образование шпинели 15	—	—

1) Temperature in degrees; 2) phases found on microscopic examination of mixture-roasting products; 3) same, with addition of 2% B_2O_3; 4) same, with addition of 2% $FeCl_3$; 5) β-Al_2O_3; α-Al_2O_3·MgO spinel (about 10%); 6) considerable quantity of β-Al_2O_3; very little MgO spinel; 7) β-Al_2O_3; MgO; α-Al_2O_3 appears, with spinel (10-15%); 8) β-Al_2O_3 has been converted to α-modification; 30-40% spinel; 9) same phases; little spinel (about 40%); 10) same phases; 15-20% spinel; 11) same phases; about 90% spinel; 12) quantity of spinel has increased; 13) very little β-Al_2O_3; 50-60% spinel; 14) no β-Al_2O_3; present are very small amounts of α-Al_2O_3 and spinel (85-90%); 15) no β-Al_2O_3; complete formation of spinel.

According to Vagner, mass transfer is effected in this reaction by diffusion of the relatively small magnesium (r = 0.74 A) and aluminum (r = 0.57 A) ions in the spinel phase, whose fixed framework is formed by relatively large oxygen ions (r = 1.36 A).

The high-temperature synthesis of spinel was studied in detail by Berezhnoy [395, 476, 477] in connection with its use for the pro-
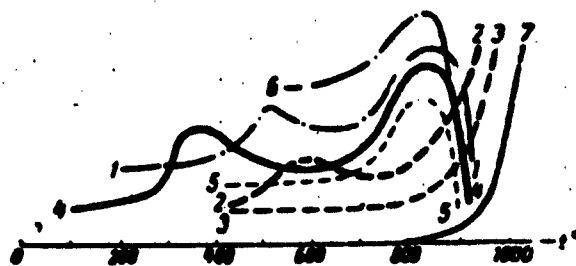
Fig. 122. Change in properties of
MgO + α-Al_2O_3 mixture in process of
spinel formation in it. 1) Hygroscop-
icity; 2) apparent heat of activation
of CO; 3) same, N_2O; 4) catalytic ef-
fect on decomposition reaction of N_2O;
5) same, on reaction $2CO + O_2 \rightarrow 2CO_2$;
6) sorption of staining yellow pigment;
7) formation of normal spinel crystals.

duction of refractory materials. He established that the formation
rate of $MgAl_2O_4$ at temperatures below 1300° is lower for mixtures with
α-Al_2O_3 than for mixtures with -Al_2O_3, and that it is almost identi-
cal in both cases at higher temperatures. The presence not only of
the boron oxide but also of iron oxides sharply raises the formation
rate of the spinel. The rate of this process is also increased when a
chromite is added to the reaction mixture. After two hours of exposure,
the starting oxides are converted completely into spinel at a tempera-
ture of 1500°, and this occurs at 1350° in the presence of iron oxides
or barium oxide [sic]. Berezhnoy and Slonimskaya [476] investigated
the synthesis of magnesium spinel and the production of refractory
products based on it from a technical raw material. It was established
here that a charge consisting of 70 parts by weight of technical
aluminum oxide, 30 parts by weight of caustic magnesite and 2 parts
by weight of chromite (Saran' deposit) is optimal for producing spinel
refractories.

The products obtained by roasting this charge at 1650° consist

- 413 -

of spinel (85%), an unreacted mass (10%) and glass (5%).

Lipinskiy [499] and certain other authors have investigated the production of aluminum-magnesium spinel by replacement of the iron in $FeO \cdot Al_2O_3$ by magnesium in the reaction

$$FeAl_2O_4 + MgO \rightarrow FeO + MgAl_2O_4$$
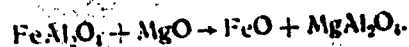
An original thermal aluminum method for producing spinel that is of interest for the production of spinel refractories was proposed in 1947 by Pevzner [500].

The basic properties of magnesium spinel are presented in Table 41. Possessing a high melting point (2135°) and high chemical stability, particularly (which is especially important) with respect to the aggressive action of various molten materials, including metallurgical slags, spinel is of exceptional interest for refractory technology. The high hardness of synthetic spinel (8) permits its use as an abrasive.

Finally, magnesium spinel forms solid solutions with a number of colored spinels. It therefore serves as the base for producing certain stable ceramic pigments. Their preparation has been studied in detail by Tumanov [501].

TABLE 43

Reaction of Chromic Oxide With Forsterite at Temperature of 1200° (change in relative quantity of reacted forsterite over time) [507]

1 Время час.	2 Фазовый состав смеси в %				Доля прореагировавшего 3 форстерита в %
	Mg_2SiO_4	$MgSiO_3$	$MgCr_2O_4$	Cr_2O_3	
0	48	—	—	52	0
0,5	40	6	11	43	17,3
1	36	9	16	39	25,0
2	32	12	22	34	33,5
4	32	12	22	34	34,2
7	30	13	25	32	38,2

1) Time, hours; 2) phase composition of mixture in %; 3) fraction of forsterite reacted, %.

- 414 -

Reaction of Chromic Oxide With Forsterite at Various Temperatures (fraction of forsterite reacted after 2 hours)

Температура 1 • град.	Фазовый состав смеси в % 2				Доля прореагировавшего форстерита в % 3
	Mg₂SiO₄	SiO₂	MgCr₂O₄	Cr₂O₃	
До нагревания 4	48	—	—	52	0
1000	44	3	5	48	8,1
1100	31	10	20	36	30,1
1200	30	13	33	24	37,2
1300	21	19	37	23	56,3
1400	13	25	48	14	72,2
1500	6	30	58	6	88,3
1600	5	31	58	6	89

1) Temperature in degrees; 2) phase composition of mixture in %; 3) fraction of forsterite reacted in %; 4) before heating.

A rather large number of investigations has been devoted to the $MgO-Cr_2O_3$ system and, in particular, to synthesis of the spinelide $MgCr_2O_4$ (picrochromite) in view of their great technical importance. These studies include those of Khedval [502], Khyutting [503], Bazilevich [475], Berezhnoy [477], Dilaktorskiy [504] and other authors.

Khyutting et al. [503] found that catalytic activity increases in a mixture of MgO with Cr_2O_3 at a temperature of 400°; the maximum of this activity is observed at 600°. The formation of $MgCr_2O_4$ at a temperature of 620° has been established by x-ray investigation, although traces of lines of this compound can be discerned on the x-ray patterns at temperatures as low as $300-400^\circ$.

Fishbek and Eyneke [505] and Yander and Shtamm [506] observed the formation of picrochromite in a mixture of MgO with Cr_2O_3 at a temperature of 1300°.

According to Berezhnoy [395], formation of $MgCr_2O_4$ takes place at a higher rate in mixtures of the crystalline reagent than that of $MgAl_2O_4$, and has gone practically to completion after two hours of

exposure at 1350°, i.e., at a temperature 150° lower than that of formation of $MgAl_2O_4$.

The rates of formation of $MgCr_2O_4$ and $MgAl_2O_4$ differ particularly widely at temperatures below 1100°. Berezhnoy accounts for this difference in terms of greater mobility of the chromium ions as compared to the aluminum ions.

Budnikov and Berezhnoy [507] prepared magnesiochromite by reacting chromic oxide with forsterite:

$$Mg_2SiO_4 + Cr_2O_3 \rightarrow MgSiO_3 + MgCr_2O_4.$$
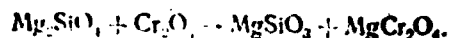
Prior to annealing, an equimolar mixture of the finely ground initial reagents — synthetic forsterite and chemically pure chromic oxide that had been roasted at 700° — were pressed under a pressure of 500 kg/cm².

It was established by the investigations that at 1200°, the reaction in such a mixture takes place relatively rapidly in the course of the first two hours, after which it is severely retarded, coming practically to a halt (Table 43 and Fig. 123) due to the high diffusion resistance of its products.

As the temperature is elevated, the rate of the process increases considerably (Table 44 and Fig. 124). In practice, the reaction may be noted at a temperature of about 900°; at t > 1300°, we observe partial formation of a glass whose composition is close to that of magnesium metasilicate; the reaction goes all the way to completion in two hours at 1850-1900° (figures found by extrapolation).

Khedval and Ni [502] produced $MgCr_2O_4$ by the reaction

$$MgO + FeCr_2O_4 \rightarrow FeO + MgCr_2O_4.$$
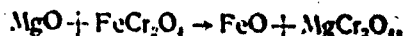
and in the reaction of magnesium oxide with natural chromite of the composition $(Fe, Mg) \cdot (Cr, Al_2)O_4$. The results of the investigation (Fig. 125) indicate that the rate of reaction of magnesium oxide with
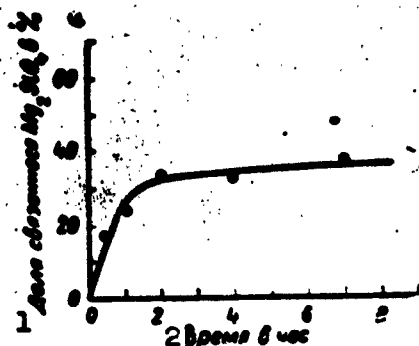
Fig. 123. Reaction of chromic oxide with forsterite at temperature of 1200° with various process times. 1) Fraction of Mg_2SiO_4 bound, %; 2) time in hours.
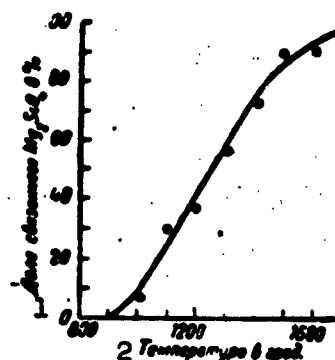

Fig. 124. Reaction of chromic oxide with forsterite at various temperatures. 1) Fraction of Mg_2SiO_4 bound, %; 2) temperature in degrees.

$FeCr_2O_4$ is considerably higher than with natural chromite. This is probably to be accounted for by the difference in the true reaction areas and, in particular, in the conditions of diffusion between the reactions of MgO with $FeCr_2O_4$ and with natural chromite; at any rate,
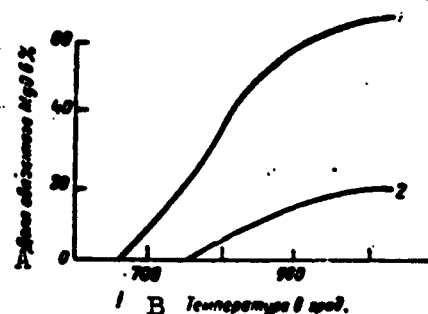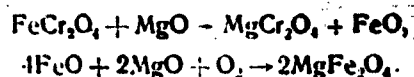

Fig. 125. Reaction of magnesium oxide with $FeCr_2O_4$ (1) and with natural chromite (2) [after Khedval]. A) Fraction of MgO bound, %; B) temperature in degrees.
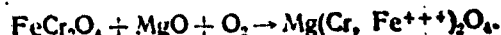
the particles of MgO and Cr_2O_3 are more widely separated.

It was established that $MgCO_3$ reacts more rapidly with chromite than does MgO. This might be linked with promotion of the diffusion process due to the loosening effect exerted on the lattice by the CO_2 literated in the dissociation of $MgCO_3$. A more rigorous explanation for this effect may be given on the basis of detailed analysis of the mechanism and kinetics of the process, taking into account the fusibility of the system formed by $MgCO_3$-MgO-(Fe, Mg)·(Cr, Al)$_2O_4$ and

- 417 -

the chromite impurities.

Berezhnoy [385], Pines [508] and other investigators have studied the reaction of magnesium oxide with $FeCr_2O_4$ both in the pure mixture and with additives of B_2O_3 or CaF_2. It was shown here that on heating of mixtures of chromite and magnesium oxide in an oxidizing medium (so-called oxidative roasting), the following reactions take place:

$$FeCr_2O_4 + MgO \rightarrow MgCr_2O_4 + FeO,$$
$$4FeO + 2MgO + O_2 \rightarrow 2MgFe_2O_4.$$

or, in the net,

$$FeCr_2O_4 + MgO + O_2 \rightarrow Mg(Cr, Fe^{+++})_2O_4.$$

Recent investigations of this process have shown that the composition of its product corresponds more exactly to the expression

$$(Mg, Fe^{++})(Cr, Fe^{+++})_2O_4.$$

Certain other conditions of preparation of magnesiochromite are also known. Thus, Krasenskaya, Yasinovskiy and Goncharov [509] prepared $MgCr_2O_4$ from the melt in a study of fusibility in the $MgO-Al_2O_3-Cr_2O_3$ system. Ryss and Uritskaya showed that in thermal dissociation of magnesium chromate, the ultimate product is $MgCr_2O_4$:

$$2MgCrO_4 \rightarrow 2MgO \cdot Cr_2O_3 + 1,5O_2 \rightarrow MgCr_2O_4 + MgO$$
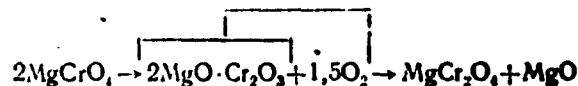
and so forth.

The properties of magnesiochromite are of direct interest for technology. $MgCr_2O_4$ crystallizes in the cubic system (lattice parameter 8.31 A), has a specific gravity of 4.4 to 4.43 and possesses a high melting point ($2330°$) and relatively high hardness (6). This mineral is used in the technology of refractory materials and ceramic pigments.

The spinelide of the composition $MgFe_2O_4$, magnesioferrite, has been known for a long time. It is rarely encountered in nature, but easily produced synthetically, for example, by roasting magnesites.

A large number of papers have been devoted in recent years to

the synthesis of this compound from the oxides. Khyutting studied the property changes of an MgO + Fe_2O_3 mixture as functions of temperature (see Fig. 126). The formation of magnesioferrite begins in such a mixture at a temperature as low as 600°. According to Berezhnoy, about 90% of the stoichiometrically possible $MgFe_2O_4$ has formed after 2 hours at 1200°. Above 1450°, as was shown by Belyankin and Chervinskiy [510], this compound undergoes marked dissociation with formation of magnomagnetite (Mg, Fe^{++}) $(Fe_2^{+++}O_4)$ and magnesiowuestite (Mg, Fe^{++})O.

A
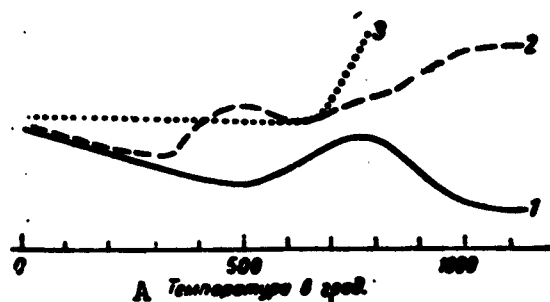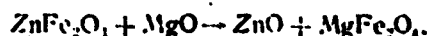
Fig. 126. Change in properties of MgO + Fe_2O_3 mixture in process of formation of $MgFe_2O_4$ [after Khyutting]. 1) solution of MgO; 2) solution of Fe_2O_3; 3) magnetic susceptibility. A) Temperature in degrees.

Magnesioferrite may also be produced by a substitution reaction, for example,

$$ZnFe_2O_4 + MgO \rightarrow ZnO + MgFe_2O_4.$$

It crystallizes in the cubic system (a_w = 8.36 A), has a specific gravity of 4.2 to 4.49 and melts (incongruently with formation of ferric oxide) at a temperature of 1750°. A singular property of $MgFe_2O_4$ is its high magnetic susceptibility (Fig. 126), which must be taken into account, for example, in work with roasted magnesite, which almost always contains a certain quantity of $MgFe_2O_4$.

Magnesioferrite is hardly worthy of special attention as an inde-

pendent refractory. However, the significance of its properties and the processes in which it is formed in the production of magnesium refractories is very great.

Among the systems containing MgO, many other spinelides and the processes in which they are produced by heating mixtures of crystalline reagents have also been studied.

Thus, Tammann [211] established by x-ray procedures the formation of $MgSb_2O_4$, which possesses a tetragonal lattice, in a mixture of MgO and Sb_2O_3 at a temperature of 500°.

Gauptman and Novak, Bart and Poznyak and other investigators synthesized $MgGa_2O_4$ ($a_w = 8.28$ A) and $MgIn_2O_4$ ($a_w = 8.81$ A), which crystallize in the cubic system.

It was established independently of the research of the above authors that lines of $MgIn_2O_4$ appear on x-ray patterns at 1250-1300° during roasting of a mixture of precipitated hydroxides of magnesium and indium.

The spinelide $MgLa_2O_4$, which has a melting point of about 2050°, has been prepared by fusion of the oxides. The formation of $MgCo_2O_4$, which crystallizes in the cubic system ($a_w = 8.107$ A), has been established, but little is known as yet concerning its properties.

Berezhnoy [395] prepared the spinelide $MgMn_2O_4$ by reaction in a crystalline mixture; here, it was established that all other conditions the same, the rate of its formation is lower than the rates of formation of $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$ and $MgMn_2O_4$; it apparently crystallizes in the tetragonal syngony, possesses direct extinction and refractive indices $N_g = 2.35$ and $N_p = 2.3$. Its specific gravity is about 4.7 and its melting point about 1700°. Exact determination of the properties of this compound is extremely difficult, since it readily undergoes partial conversion to $(Mg, Mn) Mn_2O_4$.

According to Berezhnoy's observations [511], no spinelide is formed in mixtures of $MgO + Bi_2O_3$ (even when a melt of them is crystallized). As we know, the same situation has been observed for the $CaO-Bi_2O_3$, $SrO-Bi_2O_3$ and $BaO-Bi_2O_3$ systems.

Spinelides of a somewhat different type, $Ti^{+4}Mg_2O_4$ and $Sn^{+4}Mg_2O_4$ (the formation of which is described in the next section), have been studied rather thoroughly and, as it developed, possess highly interesting properties.

The spinelide MgV_2O_4, the formation and properties of which were studied by Ryudorf and Reyter [512] and then in greater detail by Lovel [473] is also worthy of attention. This spinelide is prepared by heating tableted powdered mixtures of magnesium oxide with vanadium oxide in a pure nitrogen or hydrogen atmosphere to temperatures of 900-1100° and above. The black $MgO \cdot V_2O_3$ crystallizes in the cubic system (lattice parameter 8.39 A), has a specific gravity of 4.24 and possesses a very weak magnetic susceptibility.

Systems with CaO

The compound $CaR_2^{+++}O_4$ is not encountered in nature. The formation of various compounds of this type has been studied by many authors in connection with research on cementing materials. The work of Eyneke in this field, for example, is well known. He showed that the primary reaction product in mixtures of CaO with Al_2O_3 is $CaAl_2O_4$, regardless of the initial proportions between these oxides. This statement was subsequently confirmed by Lagerkvist et al. [513] (who also established that the crystal lattice of $CaAl_2O_4$ is not cubic), Novakovskiy and Ponirovskaya [514, 515] and other authors.

Using the Gan [Hahn] emanation method, Yagich [516] showed that calcium carbonate reacts with aluminum oxide at a noticeable rate at 600°. The surfaces of the alumina crystals are opened up considerably

before the reaction begins. At temperatures from 900 to 1000°, rapid formation of $CaAl_2O_4$ takes place. This compound melts congruently at 1600° and hence may also be prepared from a melt of the appropriate composition.

The compounds $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$ and $CaO \cdot 6Al_2O_3$* are known in the $CaO-Al_2O_3$ system.

On the basis of x-ray analysis, the formulas $9CaO \cdot 5Al_2O_3$ and $12CaO \cdot 7Al_2O_3$, which are also used comparatively rarely at the present time, were suggested for the second of these compounds.

With an adequate excess of lime in the initial mixture, $5CaO \cdot 3Al_2O_3$ makes its appearance after formation of the above primary reaction product. Yung and Butt [517] obtained this compound by reacting $CaCO_3$ with Al_2O_3 at a temperature of 1350°. With an even larger lime excess and a temperature of about 1400°, we observe formation of tricalcium aluminate ($3CaO \cdot Al_2O_3$) from the $CaO \cdot Al_2O_3$.

In the case of an excess of alumina in the reaction mixture, $CaO \cdot 2Al_2O_3$ is obtained from $CaO \cdot Al_2O_3$ at 1400° (the formula $3CaO \cdot 5Al_2O_3$ is sometimes ascribed to this compound). Tricalcium aluminate and the aluminate of composition $CaO \cdot 2Al_2O_3$ melt without decomposition, the former at 1535° (Renkin and Rayt, 1909), and the latter at 1765° [518]. At 1380°, $3CaO \cdot Al_2O_3$ and $5CaO \cdot 3Al_2O_3$ form a eutectic [515].

Calcium aluminates are present in Portland cement and alumina cement, so that they are also discussed in Chapter 10.

A compound of the composition $CaCr_2O_4$ was prepared as long ago as 1895 by Dyufo [519], who melted a mixture of CaO with Cr_2O_3 in an electric furnace for this purpose. In recent times, this compound has been synthesized by numerous authors (see, for example, [520, 521]). Sanada prepared it by roasting a mixture of these oxides.

The "coating" period in the reaction of CaO with Cr_2O_3 is detected

from the change in sorption properties of the mixture at temperatures as low as 300°. Irrespective of the proportions between the components of the initial mixture, the primary reaction product is $CaCr_2O_4$. This compound is green in color, crystallizes in the rhombic system, and has a specific gravity of 4.8; it separates from the melt in the form of needles.

Sanada also described the compount $Ca_2Cr_2O_5$, claiming to have prepared it in the solid phase at 1350°.

Vasenin [522] concluded on the basis of investigations that he had conducted that the reaction between CaO and Cr_2O_3 on heating in air first proceeds to formation of chromates (at temperatures from 600 to 800°) and then, at about 1020°, goes over to reduction of the chromates to chromites. When the mixtures are heated in air in a platinum furnace to 1400° at a rate of 10° per minute, only with the CaO and Cr_2O_3 present in 1-to-3 proportions do we obtain sinter cakes consisting of homogeneous crystals. With proportions of 0.5, 2 and 4, which corresponds to the compounds $CaO \cdot 2Cr_2O_3$, $2CaO \cdot Cr_2O_3$ and $4CaO \cdot Cr_2O_3$, on the other hand, we do not observe the formation of a homogeneous crystalline structure.

The author characterizes $CaO \cdot Cr_2O_3$ as follows. This compound consists of distinct green prismatic crystals that exhibit pleochroism (N_g' dark green, N_p' light green); the refractive indices are $N_g' = 2.33 + 0.002$, $N_p' = 2.18 + 0.002$, the melting point is 2090° (according to another source, 2170°). The compound produced on heating a mixture of CaO and Cr_2O_3 taken in 3:1 proportions is, in the author's opinion, tricalcium oxychromite of the composition $3CaO \cdot Cr_2O_5$ rather than $3CaO \cdot Cr_2O_3$.

Budnikov [520] studied the physicochemical processes that take place when the CaO in dolomite reacts with Cr_2O_3. He made up 40 dif-

ferent mixtures based on calculations for binding of these oxides into

$2CaO \cdot Cr_2O_3$, $3CaO \cdot Cr_2O_3$ and $4CaO \cdot Cr_2O_3$ and roasted these mixtures at

1500° for 20 minutes. It was established by determining the quantity

of free lime in the roasting products that the molar ratio of the re-

acted CaO and Cr_2O_3 is between 3 and 4. The extent of recrystallization

at the roasting temperature indicated above was rather high.

Zhuravlev [521] made a microscopic investigation of the sintering

products of mixtures of technically pure calcium oxide and chromic

oxide with the $CaO:Cr_2O_3$ ratio equal to 1, 2, 3 and 4. The mixtures

were roasted three times at a temperature of 1350° with holding times

of two hours. The author concluded as a result of the studies that

under the conditions of his experiments only two compositions (CaO:

$:Cr_2O_3 = 1$ and $CaO:Cr_2O_3 = 3$) produce binary compounds. The compound

$2CaO \cdot Cr_2O_3$ does not form; the roasting temperature was not high enough

for formation of $4CaO \cdot Cr_2O_3$.

The preparation processes for calcium ferrites, and $CaFe_2O_4$ in

particular, have been the subject of a very large number of research

studies (see, for example, [490, 516, 523-528]). Konarzhevskiy [523]

made a particularly extensive study in this direction in 1931.

It was established as a result of the work done that heating of

mixtures of CaO with Fe_2O_3 to 250° reduces their sorption capacity;

the deactivation maximum occurs at a temperature of 425°.

Use of the Gan emanation method enables us to note the formation

of the primary reaction product, $CaFe_2O_4$, at temperatures of from 560

to 600°. Konarzhevskiy, on the other hand, observed the reaction

taking place even at 500° in determining the free CaO.

The first lines of $CaFe_2O_4$ appear on x-ray patterns only after

the reaction mixture has been heated to a temperature above 650°;

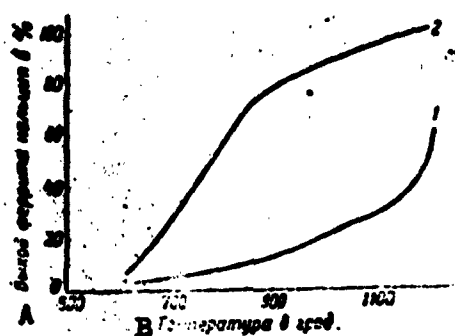correction of the lattice defects of this compound, which is produced

Fig. 127. Formation of $CaFe_2O_4$ in mixture of $CaCO_3$ with Fe_2O_3 at various temperatures and $\tau = 2$ hours. 1) Without combined grinding; 2) with combined grinding of starting materials. A) Yield of calcium ferrite in %; B) temperature in degrees.

by reaction in the crystalline mixture, is complete at a temperature of 850°.

Konarzhevskiy showed that when mixtures of calcium carbonate with ferric oxide are heated, $CaFe_2O_4$ may be formed as a result of direct reaction between the reagents:

$$CaCO_3 + Fe_2O_3 \rightarrow CaFe_2O_4 + CO_2$$

or after decomposition of the $CaCO_3$:

$$CaCO_3 + Fe_2O_3 \rightarrow CaO + CO_2 + Fe_2O_3 \rightarrow CaFe_2O_4 + CO_2.$$

He studied the influence of combined grinding of the initial reagents,

temperature and certain other factors on the process in which calcium ferrites form. His most important research results are shown in Figs. 127 and 128.
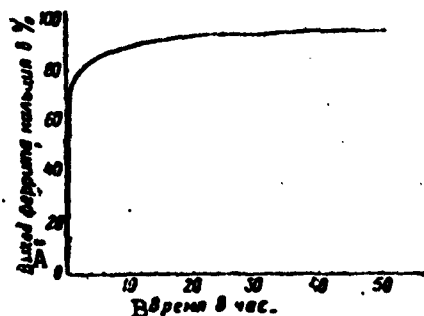

Fig. 128. Formation of $CaFe_2O_4$ in mixture of combination-ground $CaCO_3$ and Fe_2O_3 at 900° with various process times. A) Yield of calcium ferrite in %; B) time in hours.
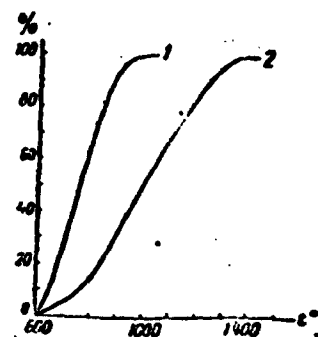

Fig. 129. Formation of $CaFe_2O_4$ (1) and $MgFe_2O_4$ (2) at various temperatures (exposure $\tau = 2$ hours at t_{max}).

The intensity of the reaction between the reagents and, accordingly, the extent to which they are converted into product during a

specific process time naturally depend on the method used to prepare the reaction mixture (Fig. 127): for example, combination grinding results in more uniform distribution of the reagents, an increase in the area of the contact surface between them and, apparently, in activation of the grain surfaces and hence acceleration of the reaction. The nature of the dependence of process rate on temperature is also related to the method of pretreatment of the reagents.

The curves of Fig. 128 permit us the conclusion that even when calcium carbonate is preground together with the ferric oxide, the rate of the over-all process at 900° and the degree of conversion of the reagents into the product above 70-75% were limited in the experiments described by the rate of internal diffusion. At small product yields, however, the diffusion resistance of the $CaFe_2O_4$ layer was obviously relatively low.

Khedval and Zandberg [528] studied reactions in mixtures of calcium oxide with ferric oxide that had been prepared by various methods ($\alpha-Fe_2O_3$ from the oxalate and sulphate of iron, $\gamma-Fe_2O_3$), and in mixtures of $Ca(OH)_2$ with $\gamma-Fe_2O_3$. It was established here that $Ca(OH)_2$ first reacts more intensively with the ferric oxide than does CaO. In accordance with our conceptions as to the intensifying influence of a liquid phase on certain conversion processes of crystalline mixtures (Chapters 3, 7), this may be accounted for by fusion of the $Ca(OH)_2$ or a eutectic that incorporates this compound.

This explanation is consistent with the fact that the difference in the rates of reaction of the reagents in mixtures of $Ca(OH)_2$ + + Fe_2O_3 and CaO + Fe_2O_3 is observed at the beginning of the process, apparently before the calcium oxide hydrate has been dehydrated.

Nagai and Ioshiura [527] established that the addition of 1% of CaF_2 to the reaction mixture accelerates considerably the process in

which calcium ferrites form in crystalline mixtures. As was shown by Berezhnoy [385], the rate of formation of $CaFe_2O_4$ in an oxide mixture is, all other conditions the same, considerably higher than that of $MgFe_2O_4$ (Fig. 129).

According to Nakken [525], $CaFe_2O_4$ belongs to the rhombic system. Gil'pert [490] assumes that the $CaFe_2O_4$ lattice belongs to a special type. This compound is ferromagnetic at temperatures below $1050°$; it melts incongruently at $1216°$.

In a certain concentration region, the compounds $CaAl_2O_4$ and $CaFe_2O_4$ form solid solutions, which were studied in detail by Belyankin, Toropov and Dyuko [529].

Systems With SrO

Compounds SrR_2O_4 are not encountered in nature and can be produced only synthetically. Their formation has not been studied as fully as that of MgR_2O_4 and CaR_2O_4 compounds.

It has been established by x-ray study of roasted mixtures of SrO with Al_2O_3 [513] that the primary product of the reaction between these oxides, formation of which may be noted at temperatures below $1000°$, is $SrAl_2O_4$. This compound, whose structure closely resembles that of $CaAl_2O_4$, was studied in detail by Toropov [530], who established its optical biaxiality and determined its refractive indices: $N_g = 1.663 + 0.02$ and $N_p = 1.649 + 0.002$. According to Vartenberg, the melting point of $SrAl_2O_4$ is $2015°$. However, this aluminate is not employed as a refractory material, since it does not possess any advantages over other more readily available substances that have the same refractory properties.

The compound $SrCr_2O_4$ has been studied on many occasions. Nevertheless, the process in which it forms and its properties have not been studied to this day. One reason for this is the rather intensive oxi-

dation of chromic oxide to chromic anhydride in the presence of SrO by oxygen; as a result, synthesis of $SrCr_2O_4$ in an atmosphere of air is difficult and the reaction product contains a certain quantity of hexavalent chromium.

The preparation of strontium ferrites, primarily $SrFe_2O_4$ in mixtures of strontium carbonate with ferric oxide, has been known for over 30 years [531].

It follows from the work of Forestier and other authors [523, 531-534] that $SrFe_2O_4$ forms at temperatures below $1000°$, apparently as the primary reaction product. This compound crystallizes in the hexagonal system. Its magnetization factor is considerably smaller than, for example, that of $MgFe_2O_4$.

The properties of strontium ferrite preparations obtained from various starting materials differ somewhat from one another; thus, the specific gravity of the compound produced from $SrCO_3$ and Fe_2O_3 is 4.966, while that obtained from SrO and Fe_2O_3 shows 5.05.

The compound $SrFe_2O_4$ forms a range of solid solutions terminating in the composition $SrO \cdot 9Fe_2O_3$ [534]. The technical importance of strontium ferrites is as yet minor.

Systems With BaO

Compounds BaR_2O_4 are not known in nature; they are obtained by synthesis. Barium aluminate $BaAl_2O_4$ was synthesized long ago, both by the reaction in the mixed crystalline solids and by fusion. However, the first detailed description of the properties of this spinelide was published by Toropov [535] only in 1935. Somewhat later, Grube and Geynts [536] studied the formation of $BaAl_2O_4$ in a crystalline mixture, while Val'mark and Vestgren [537] studied its properties.

The compound $BaAl_2O_4$ is the primary reaction product, and, on heating to about $1050°$, the only one in mixtures of barium oxide with

aluminum oxide. The reaction between these oxides to form the aluminate takes place rather rapidly at temperatures below 900°.

$BaAl_2O_4$ may also be obtained by the reaction

$$BaSO_4 + Al_2O_3 \rightarrow BaAl_2O_4 + SO_2 + \frac{1}{2}O_2$$

which was studied by Avgustinik and Mchedlov-Petrosyan [538]. This reaction takes place at a noticeable rate at temperatures above 1000°. Its heat effect is 143.54 kcal/mole, while the heat of the reaction $BaO + \gamma\text{-}Al_2O_3 \rightarrow BaAl_2O_4$ is only 4.24 kcal/mole.

$BaAl_2O_4$ crystallizes in the hexagonal system; its refractive index is about 1.683, and its melting point 1820° (2000° according to Vartenberg) [535].

Barium aluminates have a very important part in the chemistry of the oxide cathode and are of a certain amount of interest as refractory cements for highly specialized applications.*

Barium chromite has been synthesized many times by reaction in the crystalline mixture. In this case, however, as with the synthesis of chromite in the $SrO\text{-}Cr_2O_3$ system, a certain quantity of hexavalent-chromium compounds readily form in an atmosphere of air. This makes it difficult to study the formation reaction of $BaCr_2O_4$ and its properties.

The synthesis of barium ferrites has been the object of numerous investigations (see, for example, [524, 537, 539]). Ershak et al. made a particularly detailed study in this direction [540]. They studied the progress of the reaction in mixtures of barium carbonate with ferric oxide containing from 10 to 99% of $BaCO_3$ at temperatures from 500 to 1000°.

It has been established by x-ray analysis that the compound $BaO \cdot 2Fe_2O_3$ forms in a reaction mixture of the corresponding composition at temperatures above 550°; $BaO \cdot 6Fe_2O_3$ (the familiar analog of

"β-Al$_2$O$_3$") appears in mixtures containing from 5 to 40% of BaCO$_3$ at temperatures above 750°; with contents of 50-95% BaCO$_3$ in the mixture and a temperature above 800°, the result is formation of a compound whose composition probably corresponds to Ba$_8$Fe$_8$O$_{21}$ (with an oxygen deficiency in the elementary cell); its structure is similar to that of perovskite, whose elementary cubic cell has a side 8.05 A long.

Thus, Ershak did not produce the compound BaFe$_2$O$_4$, while, according to communications of Forestier [524 and others], the latter not only succeeded in preparing this compound, but also studied its properties. According to this author, BaFe$_2$O$_4$ crystallizes in the hexagonal system and is similar to SrFe$_2$O$_4$ as regards its properties.

TABLE 45

"Onset" Temperature of Substitution Reaction
for Divalent Oxides in Spinelides (in degrees)

Замещающий окисел [1]	Соединения [2]				
	Zn Al$_2$O$_4$	CoAl$_2$O$_4$	CoCr$_2$O$_4$	FeCr$_2$O$_4$	CuAl$_2$O$_4$
CaO	475	450	510	500	760
SrO	425	435	405	405	420
BaO	345	350	300	345	370

1) Substituting oxide; 2) compound.

Further research will obviously be necessary to account for the causes of this contradiction in the results of Forestier and Ershak

TABLE 46

Influence of Gaseous-Phase Composition on Rate
of Substitution Reaction of CoO in CoCr$_2$O$_4$ by
Oxides of Group II Elements

1 Замещающий окисел	2 Степень превращения CoCr$_2$O$_4$ в % к теоретической 3 в среде	
	N$_2$	O$_2$
CaO	2,1	1,8
SrO	3,1	21,5
BaO	5,7	35,7

1) Substituting oxide; 2) degree of conversion
of CoCr$_2$O$_4$ in % of theory; 3) in medium of.

and eliminate them.

Khedval's data [214] on the "onset" temperatures of substitution reactions of divalent oxides in compounds MeR_2O_4 by oxides of alkaline-earth metals are worthy of attention (Table 45). The variation of these temperatures over a relatively narrow range for SrO and BaO and over a wide range for CaO is also in agreement with the above ($4, Chapter 3) conceptions as to the possible role of a liquid phase in reactions of this type, although the very concept of reaction "onset" temperature is, naturally, arbitrary.

Khedval showed that the rate of substitution reactions in mixtures containing substances whose compositions incorporate elements of variable valency depends on the composition of the atmosphere in which the reaction is taking place. It follows from the data that he obtained (Table 46) that the influence of gaseous-phase composition on the rate of the process is different for oxides of different group II elements: it is virtually unnoticeable for CaO, while it is quite significant in the cases of SrO and BaO.

This difference may be accounted for in terms of the nonidentical conditions for diffusion in the different systems, which are due to the physical properties of its components.

Recently, as we know, the mechanism by which gaseous-phase composition influences various reactions in crystalline mixtures (particularly mixtures containing compounds of variable-valency elements) has been examined in many investigations (see, for example, [131, 215, 260, 541]).

Systems With ZnO

The formation of zinc spinelides in crystalline mixtures has been studied in very great detail, chiefly as a result of the convenience with which systems containing ZnO can be subjected to ex-

perimental research. It was on the basis of data pertaining to these systems that Khyutting formulated his concepts as to the periods or stages in reactions in solid mixtures (§1, Chapter 3).

Above (pages 157-159), we presented detailed data on reactions in the $ZnO-Fe_2O_3$ system [204, 205]. Since other systems with ZnO are to a certain degree analogous to it, we may omit here any detailed examination of intermediate reaction periods in the formation of the various zinc spinelides in crystalline mixtures.

Zinc aluminate $ZnAl_2O_4$ or gahnite is encountered in nature. It was produced synthetically from melts even in the XIX Century. Subsequently, detailed study was devoted to its preparation in crystalline mixtures in the absence of liquid phases (see, for example, [220, 224, 396, 501, 542, 543]). Formation of this spinelide was noted by x-ray means [220] in a mixture of the oxides at 700°; at 800° after 5 hours and 30 minutes, the yield may be 60% [396], but less than 50% at a temperature of 900° after 2 hours [544], both figures applying to the theoretically possible quantity of $ZnAl_2O_4$. According to other sources [545], at 1000° almost total conversion of these reagents into the product is achieved only after 99 hours. All of these data are, of course, characteristic of definite (and different) experimental conditions.

The first attempt to investigate the mechanism of this process was undertaken by Khil'd [546]. Khil'd accounted for the progressive weakening of the Al_2O_3 lines that he observed on x-ray patterns cast by specimens of mixtures roasted at temperatures of 975° (the intensity of the ZnO lines remained unchanged) in terms of preferential movement of ZnO in the spinel layer. Actually, Khil'd's experiments established only that a spinel layer forms on the corundum. We have available a more circumstantial characterization of this mechanism in the pub-

lished results of Bengston and Yagich [224].

Assuming that the Vagner apparatus (see Fig. 41) would be useless in this case because of the low rate of diffusion of ions in spinel, Bengston and Yagich employed the interface-marking technique. To the tablet surfaces of one or both reagents (α-Al_2O_3 and ZnO), the authors applied a "tag" made of platinum black — a substance that would be visible under the microscope but would not interfere with contact between the reagents or react with them chemically.
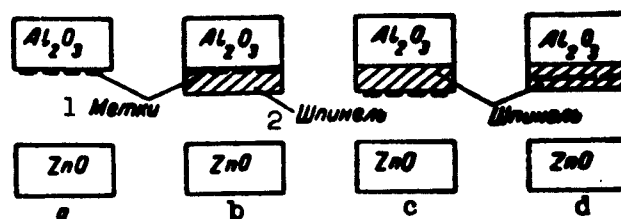

Fig. 130. Marking of Al_2O_3 tablets after Bengston and Yagich. Position of mark: a) before experiment; b) after experiment with displacement of Al^{3+} ions and electrons practically exclusive; c) after experiment with displacement of Zn^{2+} ions and electrons practically exclusive (in either case, displacement of oxygen takes place through the gaseous phase); d) counterdiffusion of Zn^{2+} and Al^{3+} ions in equivalent quantities according to Vagner scheme. 1) Mark; 2) spinel.

Depending on the type of diffusing agent and the ratio between the diffusion rates, we might, theoretically, envision various positions of the mark as a result of diffusion (Fig. 130).

Actually, however, the order of arrangement of the layers — Al_2O_3/Al_2ZnO_4/Pt/ZnO (Fig. 131) — indicated that mass transfer takes place in this case preferentially by migration of zinc and oxygen ions or Zn^{++} and electrons.

Simultaneously, study of the process kinetics in the temperature range from 1250 to 1380° with experiment times up to 24 hours enabled
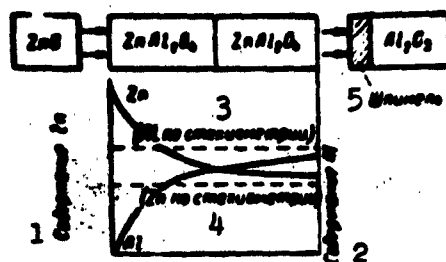
Fig. 131. Diagram showing distribution of zinc and aluminum concentrations in $ZnAl_2O_4$ tablets on reaction of ZnO with Al_2O_3. 1) Content of Zn; 2) content of Al; 3) Al by stoichiometry; 4) Zn by stoichiometry; 5) spinel.

the authors to confirm their conception as to its mechanism. However, the process in this system is complicated by noticeable sublimation of ZnO from the zinc oxide and from the spinel: the Zn vapor pressure above these compounds is quite significant at the temperatures indicated above. If we proceed from the conception of vaporization of the ZnO and preferential motion of the Zn^{2+} ions (accompanied by migration of oxygen through the atmosphere), the distribution of the zinc and aluminum concentrations in the $ZnAl_2O_4$ tablets of the system under consideration will correspond to the diagram presented in Fig. 131.

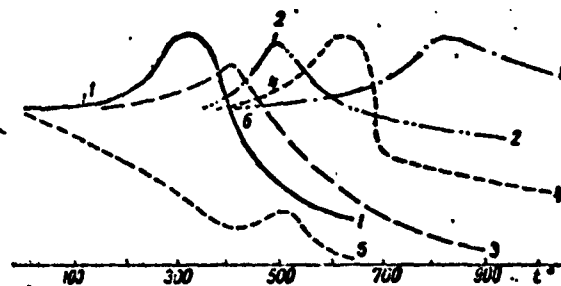Zinc aluminate crystallizes in the cubic system (a_0 = 8.09 A),

Fig. 132. Change in properties of ZnO + Cr_2O_3 mixture as a function of temperature (after Khyutting [204]). 1) Catalytic effect on decomposition of CH_3OH; 2) solubility in hydrochloric acid; 3) sorption of methylene blue; 4) sorption of fuchsin; 5) conductivity; 6) solubility in concentrated sulfuric acid.

has a refractive index of 1.805 and melts at a temperature of 1930°. As a refractory material, however, it is not, on the basis of its proper-

ties, of any particular interest. Solid solutions of $ZnAl_2O_4$ with other highly colored spinelides (cobalt and nickel spinelides and the like) would be of much greater interest. Such solid solutions (which were studied by Tumanov [501] and others) are surpassing ceramic dyes that are distinguished by high stability.

Numerous studies have been devoted to synthesis of $ZnCr_2O_4$ from the oxides. Even in the last century, this compound was produced by fusing ZnO and Cr_2O_3 together in the presence of mineralizers [480]. Its formation in a mixture of the pure crystalline oxides was studied later [220, 483, 542, 544-546].

According to Khyutting [204], the properties of ZnO + Cr_2O_3 mixtures vary with temperature (Fig. 132). Formation of $ZnCr_2O_4$ in such a mixture is detected by x-ray examination at temperatures of about $650°$. It was established by research [204] that the rate of formation of $ZnCr_2O_4$ depends on the reaction atmosphere. The process is accelerated considerably in the presence of fluxing mineralizers; with contents of, for example, potassium chloride in the reaction mixture, the reaction goes rapidly at a temperature of $1000°$. This spinelide crystallizes in the cubic system ($a_0 = 8.32$ A), is greenish-gray in color and can be used as a ceramic pigment.

The synthesis of the zinc ferrite mentioned above — franklinite — has been studied on many occasions (see, for example, [205, 220, 338, 483, 493, 542]); one aspect described in detail was the sequence of transformations and the property changes of the ZnO + Fe_2O_3 mixture (see §1 of Chapter 3). Hence it will be sufficient here to limit ourselves only to the briefest of remarks concerning the formation of $ZnFe_2O_4$.

On powder diagrams, lines of this compound are observed in the reaction mixture at roasting temperatures as low as $650°$. Franklinite

is brown in color, crystallizes in the cubic system (a = 8.42 A) and has a specific gravity of 5.32.

The properties and preparation conditions are also known for certain other zinc spinelides, such as $ZnGa_2O_4$ and $ZnSb_2O_4$.

Systems With CdO

Cadmium spinelides are not known in nature. They are prepared by reactions in crystalline mixtures. However, these reactions have been the subject of much less study than the formation reactions of the corresponding zinc compounds.

Cadmium aluminate $CdAl_2O_4$ was synthesized by Shtrassen [544]. This compound is rather unstable and decomposes at a temperature of 1350°.

Natta and Passerini [542] synthesized the tetragonal $CdIn_2O_4$, the structure of which is similar to that of $CaIn_2O_4$.

The preparation of cadium chromite has been studied in a number of investigations (see, for example, [483, 547]). This compound is light green in color and has the structure of spinel ($a_0 = 8.56$).

Cadmium ferrite $CdFe_2O_4$ has also been prepared and investigated by many authors [492, 524, 548 and others]. Heating to a temperature of 450° results in no discernible property changes in the CdO-and-Fe_2O_3 mixture. Its color begins to change only at temperatures above $450-500^\circ$; a catalytic effect on the decomposition process of nitrous oxide may be observed at temperatures from 500 to 550°. $CdFe_2O_4$ is known in two modifications [524]: paramagnetic cubic (spinel type) and ferromagnetic hexagonal (of the same type as strontium and barium ferrites).

Cadmium spinelides do not as yet have any technical value.

Systems With PbO

Lead aluminate $PbAl_2O_4$ was prepared and studied by Geller and Bunting [549] in an investigation of equilibria in the PbO-Al_2O_3 sys-

tem (formation of this spinelide in the solid mixture has not yet been studied). As follows from Fig. 133, $PbAl_2O_4$ is the only compound in this system. At a temperature of $970°$, it is converted into corundum and glass. This compound crystallizes in the hexagonal system and exhibits the refractive indices $N_0 = 1.91$ and $N_e = 1.85$.
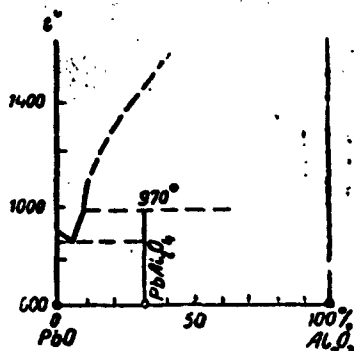

Fig. 133. Diagram of state of $PbO-Al_2O_3$ system [549].

Kittel' [547] studied the behavior of a PbO-and-Cr_2O_3 mixture on heating. An apparent result was the formation of $PbCr_2O_4$.

Lead ferrites are of considerable interest, particularly for metallurgy. $PbFe_2O_4$ can be prepared either by fusing the oxides together or by reacting them in a solid mixture [524, 543, 548]. This compound, which crystallizes in the hexagonal system after the $SrFe_2O_4$ and $BaFe_2O_4$ type, forms solid solutions with Fe_2O_3 right up to the composition $PbO·9Fe_2O_3$ [534]. Unlike many other ferrites (e.g., calcium ferrites), lead ferrite melts possess extremely high viscosity.

Systems With MnO

Manganese spinelides are known in nature in the form of the minerals galaxite ($MnAl_2O_4$) and hausmanite ($MnMn_2O_4$). The first of these can be obtained either from the melt or by reaction in a crystalline mixture. It follows from the diagram of state of the $MnO-Al_2O_3$ system [550] presented in Fig. 134 that $MnAl_2O_4$ is the only chemical compound in this system. Krauze and Til [483] prepared this compound by reaction in a mixture of oxides at a temperature of $1000°$. It is a typical spinelide, crystallizing in the cubic system (a = 8.26 A), and melts incongruently at a temperature of $1560°$. The specific gravity of galaxite lies between 3.57 and 4.23 according to various
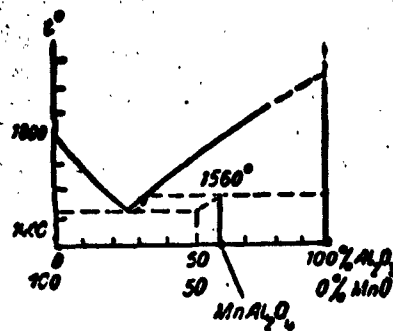
Fig. 134. Diagram of state of MnO-Al$_2$O$_3$ system [550].

The formation conditions and proper-ties of MnSb$_2$O$_4$, which crystallizes in the tetragonal system, have been the ob-ject of very little study.

All conditions the same, the rate of formation of MnCr$_2$O$_4$, which crystallizes in the cubic system with a$_0$ = 8.42 A, is considerably higher than that for MnAl$_2$O$_4$.

Hausmanite, $Mn^{+++}Mn_2^{++}O_4$ = Mn$_3$O$_4$, may be produced by heating crystal-line manganese dioxide:

$$3MnO_2 \rightarrow Mn_3O_4 + O_2;$$
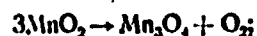
the reaction takes place in several stages; the Mn$_3$O$_4$ obtained crys-tallizes in the tetragonal system (special lattice type). Study of the properties and formation conditions of this compound is important for the metallurgy of manganese.

Manganese ferrite MnFe$_2$O$_4$ (Jacobsite) is usually produced by react-ing the crystalline oxides [483, 490, 493, 542]. Its rate of formation is low, according to Krauze [483] at 900°. The compound MnFe$_2$O$_4$ is dark brown in color, crystallizes in the cubic system (a = 8.55 A) after the spinel type, and has a specific gravity of 5.03.

Since manganese spinelides can undergo oxidation, they are, as a rule, unstable in air at high temperatures. As we noted above, they are of interest chiefly for the metallurgy of manganese.

Systems With FeO

Spinelides of divalent iron are encountered quite often in nature in the form of the minerals hercynite FeAl$_2$O$_4$, chromite (approximately FeCr$_2$O$_4$) and magnetite $Fe^{++}Fe_2^{+++}O_4$. Except for the latter, which is encountered in pure form, natural iron spinels are solid solutions

- 437 -

of two or more spinelides. Synthesis of iron spinelides is accomplished
by heating the appropriate crystalline mixtures in a reducing or
neutral medium.

The diagram of state of the FeO-Al_2O_3 system [551], as will be
seen from comparison of Figs. 135 and 134, is more complex than that
of the MnO-Al_2O_3 system. Hercynite was obtained by Krauze [483] in
the form of a brownish-red sinter cake by reacting the crystalline
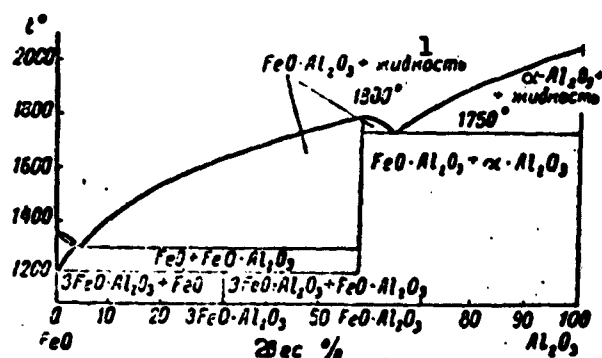oxides in a reducing medium at a temperature of 1100° for 2 hours.

Fig. 135. Diagram of state of FeO-
Al_2O_3 system [487, 551]. 1) Liquid;
2) per cent by weight.

Studying changes in the FeO-Al_2O_3 system, Fisher and Gofman [552]
established that the diffusion rate of aluminum ions through $FeAl_2O_4$
is greater than that of Fe ions in Al_2O_3. $FeAl_2O_4$ crystallizes in the
cubic system. As established by Galakhov [487], this compound melts
congruently at 1800°. The FeO-Al_2O_3 system has a eutectic between
hercynite and aluminum oxide that melts at 1750°; its composition is
36% FeO and 64% Al_2O_3 [487].

While the spinelides FeV_2O_4 and $FeSb_2O_4$ are known (the latter
crystallizes in the tetragonal system), neither has been the subject
of much study.

The chromite of divalent iron, $FeCr_2O_4$, was produced synthetically
even in the last century [480]. Krauze and Til' [483] established that

- 438 -

in a reducing atmosphere, this compound forms in the appropriate crystalline mixtures at a temperature of $800°$.

Since the melting point of this spinelide exceeds $2000°$ and it is encountered in nature (although not in the pure state) in large quantities, it has acquired great importance in the technology of refractory materials. As a result, the conversions that it undergoes have been the subject of minute study.

The natural chromite represents a solid solution of the composition $(Fe, Mg)(Cr, Al)_2O_4$. As we noted earlier, magnesium oxide may substitute the ferrous oxide in this solution in reactions in crystalline mixtures [502]. Detailed investigation of this substitution reaction, which is important for the production technology of chromomagnesite refractories, was made by Pines et al. [508].

In connection with problems that arose in the technology of these refractories, Lovel and others [553] studied the reactions

$$FeO + MgAl_2O_4 \rightleftarrows FeAl_2O_4 + MgO,$$
$$FeO + MgCr_2O_4 \rightleftarrows FeCr_2O_4 + MgO.$$
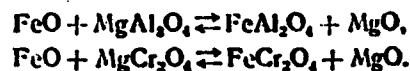
The reaction mixtures were heated for two hours at a temperature of $1400°$ in a nitrogen medium, after which microscopic and x-ray studies were made on the preparations obtained and the content of free ferrous oxide in them determined. It was found as a result that with the conditions indicated, about 0.5 mole of $FeAl_2O_4$ forms by the first reaction in the presence of 1 mole of ferrous oxide, while 0.65 mole of $FeCr_2O_4$ forms in the latter after dynamic equilibrium has been established.

The spinelides $MgAl_2O_4$, $FeAl_2O_4$ and $MgCr_2O_4$ form solid solutions of unlimited concentration, just as do MgO and FeO.

Solid solutions of spinel and chromite were studied by Goncharov and Kleynberg [554]. Formation of a continuous series of solid solu-

tions was established in this study by microscopic and x-ray investigation of roasting products of the corresponding mixtures. Goncharov et al. [555] also pointed out the high promise of such solid solutions for use in refractory-material production.

Magnetite $Fe^{++}Fe_2^{+++}O_4$ is easily obtained artificially, both from melts [480] and by reactions in solid mixtures. It is also prepared (although not in perfectly pure form) in the oxidation process of iron at high temperatures. This compound is, as we know, the basic substance in a highly important iron ore that is processed in enormous quantities by the metallurgical industry. It is also used for the manufacture of special-purpose electrodes.

The formation of solid solutions of magnetite with chromium spinelides is one of the most important causes of attrition of chromium-containing refractories in service in metallurgical furnaces. This process has been studied in minute detail (see, for example, [556]), and it has been established that growth of chromium-spinelide crystallites takes place during formation of the solid solution with Fe_3O_4. As a result, volume changes and internal stresses arise in the refractory products, leading to chipping away of the working zones of furnace liners made from chromite-containing refractories.

Systems With CoO

Many investigations have been devoted to the synthesis of cobalt spinelides.

Cobalt aluminate is prepared by reacting the oxides either with or without fluxes. In the former case, 75% of the stoichiometrically possible $CoAl_2O_4$ is formed in two hours at a temperature of 1000°, and in the latter case the reaction goes to 100% in the same time, all other conditions the same.

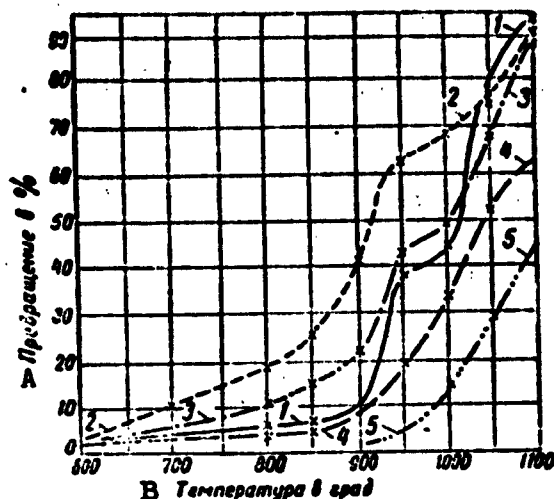Khedval and Leffler [557] investigated the rate of formation of

Fig. 136. Influence of certain factors on the process of formation of $CoAl_2O_4$ in oxide mixtures. 1) $CoO + Al_2O_3$ (preliminary four-hour processing of individual oxides at $800°$) in N_2, $\tau = 15$ minutes; 2) $Co_3O_4 + Al_2O_3$ (4 hours, $800°$) in N_2, $\tau = 15$ min; 3) $Co_3O_4 + Al_2O_3$ (4 hours, $800°$) in O_2, $\tau = 15$ min; 4) $CoO + Al_2O_3$ (4 hours, $800°$) in N_2, $\tau = 5$ min; 5) $CoO + Al_2O_3$ (4 hours, $1100°$) in N_2, $\tau = 15$ min. A) Conversion in %; B) temperature in degrees.

$CoAl_2O_4$ at temperatures of 800-$1100°$ by the reactions

$$CoO + Al_2O_3 = CoAl_2O_4.$$

$$Co_3O_4 + 3Al_2O_3 \rightarrow 3CoAl_2O_4 + \frac{1}{2}O_2$$
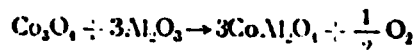
as a function of prior heat treatment of the reagents. It was established here first of all that there is a considerable rise in the rate of reaction in the temperature range from 900 to 1100° (Fig. 136), corresponding to transition of the aluminum oxide from the γ- into the α-modification. The increase in reaction rate as the temperature is

elevated further is considerably slower.

Figure 136 indicates a considerable drop in the activity of Al_2O_3 that has been roasted at 1100° (curve 5) as compared with the oxide roasted at 800° (curve 1), as well as a considerably higher activity for CoO obtained by dissociation of Co_3O_4 during the reaction process (curves 2 and 3) as compared with CoO prepared in advance. Proceeding from the conception of Co_3O_4 dissociation by the scheme

$$Co_3O_4 \rightleftarrows 3CoO + \frac{1}{2}O_2,$$

it is also easy to account for the difference in the formation rates of the final product in oxygen (curve 3) and nitrogen (curve 2) media.

The data of Khedval and Leffler can be fully explained in terms of the difference in the perfection and, hence, stability of reagent lattices produced under different conditions.

As concerns the properties of $CoAl_2O_4$, this compound, which is blue in color, crystallizes in the cubic system and possesses a high refractive index (above 1.76); it melts at a temperature of 1960° and can be counted among the superior ceramic pigments.

As is the case with cobalt aluminate, synthesis of cobalt chromite $CoCr_2O_4$ has been studied on many occasions. At a temperature of 1000° and two hours' exposure, a considerable amount of the blue-green $CoCr_2O_4$, which crystallizes in the cubic system, is observed to form in a mixture of the oxides.

Cobalt ferrite $CoFe_2O_4$ can be prepared by reaction in a mixture of the crystalline reagents and by boiling the precipitated hydroxides. This substance is grayish-black in color and also crystallizes in the cubic system.

The spinelides also include Co_3O_4. Like cobalt chromite, this compound is used in the production of ceramic pigments; however, it also has other technical applications.

- 442 -

Systems With NiO

Nickel aluminate $NiAl_2O_4$ is produced by reaction in a mixture of the crystalline oxides and by heating the precipitated hydroxides. The color of a mixture of NiO with Al_2O_3 is gray on heating to a temperature of 690° and then (at 730°) becomes light green; the mixture darkens as the temperature is further elevated.

Noticeable formation of $NiAl_2O_4$ takes place at a temperature of 700°; lines of this compound have been identified on x-ray patterns at 1000°. At 1100°, we note complete reaction of the oxides to form this spinelide.

Tersk and Uaytmor [Whitemore] [558] drew attention to the role taken by the gaseous phase (vaporization of the aluminum oxide and its migration in the vapor state to the NiO surface) in high-temperature reactions between these oxides.

The compound $NiAl_2O_4$ crystallizes in the cubic system (a = 8.04 A), has a refractive index of 1.875, melts at a temperature of 2020°, and forms solid solutions with both NiO and Al_2O_3.

It has been established by x-ray investigation that there is only a single compound, $NiCr_2O_4$, in the NiO-Cr_2O_3 system. It is obtained chiefly by reacting the oxides. It was established that Ni and Cr_2O_3 have low solubilities in $NiCr_2O_4$ at a temperature of 1100°.

Khaufe and Psher [279] investigated the mechanism and kinetics of formation of nickel-chrome spinel. Tablets of NiO, $NiCr_2O_4$ and Cr_2O_3 were put together as shown in Fig. 137. The experiments were run for 200 hours at a temperature of 1100°. Vaporization of Cr_2O_3 and a considerable mobility of the chromium ions were noted here; no migration of the nickel atoms whatever was observed.

The Cr_2O_3 layer lost weight, the spinel layers showed practically (taking evaporation losses of Cr_2O_3 into account) no change, and the

- 443 -

TABLE 47

Change in Weight of Tablets (in mg) in NiO-Cr_2O_3 System at t = 1100°, τ = 200 hours (except for*)

NiO	NiCr$_2$O$_4$	Cr$_2$O$_3$	NiO	NiCr$_2$O$_4$	Cr$_2$O$_3$
+0.6	−2.3	−2.4	+1.3	+0	−1.0
+0.1	−1.8	−2.4	+1.6	+0	−1.0
+0.2	−1.3	−2.3	+1.2	−0.4	−1.6
+1.1	−3.9	−5.3	+4.0	+0.5	−3.9*

*τ = 400 hours.

weight of the NiO tablet increased (Table 47) due to formation of a new layer of NiCr$_2$O$_4$ on the surface facing the spinel.

The authors offer the following explanation for the results that they obtained (Fig. 137). The Cr$_2$O$_3$ evaporates from the surface of the tablet 4 and condenses in the air atmosphere on the surface of the spinel layer 3 turned toward the tablet 4. This is followed by diffusion of chromium ions and migration of electrons in layers 3 and 2 in the direction of the surface of layer 2, which faces the NiO tab-
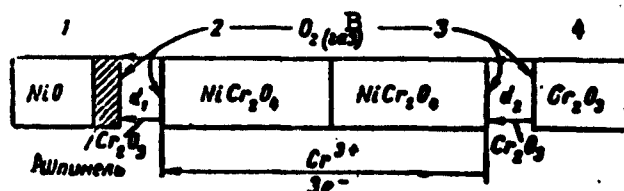
Fig. 137. Possible formation mechanism of NiCr$_2$O$_4$ from the oxides in an atmosphere of air at a temperature of 1100° (after Khaufe and Psher). 1-4) tablets. A) Spinel; B) gas.

let. Here, reacting with the gaseous-phase oxygen, the chromium forms Cr$_2$O$_3$, which then evaporates and diffuses through the gaseous phase to the surface of the NiO. This is followed by reaction between the oxides to form the spinel.

Nickel ferrite is encountered rarely in nature (in meteorites) in the form of the mineral trevorite NiFe$_2$O$_4$. It is also prepared syn-

thetically from the crystalline oxides (with slight formation of $NiFe_2O_4$ noted at a temperature of 900°) and by boiling the precipitated hydroxides in water. This compound is reddish brown (with violet overtones) and crystallizes in the cubic system ($a_0 = 8.31$ A).

The optical properties of the spinelides described — the aluminates, chromite and synthetic ferrite of nickel — were studied in detail by Dilaktorskiy.

Tumanov produced the spinelide $NiCo_2^{+++}O_4$ by reaction in a crystalline mixture. The oxide Ni_3O_4, which also belongs to this group of spinelides, is also known.

§3. TITANATES, STANNATES AND ZIRCONATES

Titanates have recently acquired considerable importance in the ceramic industry. Consequently, the processes of their formation in crystalline mixtures are of immediate practical interest. They have been studied in reports by Khedval and Tsveygberk [559], Pukal [560], Vartenberg [561], Berezhnoy [1], Keler et al. [562] and other authors.

It is known from these studies that four compounds exist in the $BaO-TiO_2$ system: $BaTiO_3$, $BaTi_2O_5$, $BaTi_3O_7$ and $BaTi_4O_9$ and, apparently, a solid solution of the subtractional type, TiO_2 in $BaCO_3$.

According to certain sources*, the formation of barium metatitanate in a mixture of barium carbonate with titanium dioxide may be observed at a temperature of 550°. At temperatures from 850 to 900° (according to Khervud and Klezens [563] at a temperature of 1200°), this process goes to completion within an hour. Keler and Vaytkus [562], who studied the changes in phase composition of the roasting products of a mixture of $BaCO_3$ with TiO_2 (1:1) on gradual heating, observed marked formation of titanates in it beginning at 830°. Here, the roasting products were the metatitanate and orthotitanate of barium. Subsequently, Keler and Karpenko [562] showed that even 30 hours of

exposure of a BaO + 2TiO$_2$ mixture results in formation of a hetero-
geneous product consisting of BaTiO$_3$, BaTi$_2$O$_5$ and BaTi$_3$O$_7$. Here, the
product obtained by synthesis at temperatures up to 1200° is a mixture
of BaTiO$_3$ and BaTi$_3$O$_7$ with a small content of BaTi$_2$O$_5$, while above
1200° it contains only BaTiO$_3$ and BaTi$_2$O$_5$. At a temperature of 1230°,
the barium trititanate begins to decompose. The rate and extent of its
decomposition increase significantly with temperature, so that after
roasting for four hours at a temperature of 1320°, a mixture containing
70% of TiO$_2$ contains only the decomposition products of barium tri-
titanate — the dititanate BaTi$_2$O$_5$ and the tetratitanate BaTi$_4$O$_9$ [562].
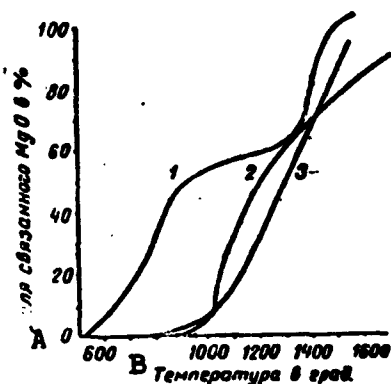

Fig. 138. Reaction of
magnesium oxide with
titanium dioxide, ti-
tanomagnetite and stan-
nic oxide. 1) Mixture
of 2MgO + TiO$_2$; 2) 30%
MgO + 70% titanomag-
netite; 3) 2MgO + SnO$_2$.
A) Fraction of MgO
bound in %; B) temper-
ature in degrees.

Among these compounds, the most de-
tailed study has been devoted to barium
metatitanate, which has a density of 5.88
g/cm^3 and is widely known as a ferroelec-
tric, i.e., a material in which polariza-
tion arises spontaneously in the absence
of an external field. BaTiO$_3$ possesses a
structure of the perovskite type and has
a cubic lattice with an elementary-cell
parameter of 4.01 A at temperatures above
the Curie point (120°). At the temperature
of 120°, a phase transition (apparently of
the first kind) takes place, with the re-
sult that the lattice becomes tetragonal
with a ratio c/a > 1 between the lengths

of the elementary-cell sides. At temperatures of 0° and (−70°), the
spontaneous polarization of BaTiO$_3$ changes direction, and phase
transitions also occur. At temperatures below 0°, BaTiO$_3$ has an ortho-
rhombic symmetry, while below (−70°) it has a monoclinic (or triclinic)

symmetry.

Barium dititanate, which has a density of 5.04, crystallizes in the monoclinic syngony, while the tri- and tetratitanates, which have the respective densities 4.75 and 4.5 g/cm^3, crystallize in the rhombic syngony [562].

Three compounds are known in the MgO-TiO_2 system: Mg_2TiO_4, $MgTiO_3$ (geikielite) and $MgTi_2O_5$. The reaction between titanium dioxide and magnesium oxide in an equimolar mixture (1:1) takes place with formation chiefly of magnesium metatitanate [562]. Running the reaction in a mixture of $2MgO + TiO_2$ at various temperatures, Berezhnoy [1] observed the appearance of a highly indicative break on the curve of magnesium-oxide binding versus temperature (Fig. 138). In the author's opinion, this break can be accounted for by the reaction of the magnesium metatitanate formed previously with the magnesium oxide at a temperature of 1000-1200°.

TABLE 48

Binding of Calcium Oxide in Formation of $CaTiO_3$ in Mixture of $CaCO_3 + TiO_2$

1 Продолжительность процесса в час.	2 Свободная окись кальция (в %) при температурах в град.		
	1100	1200	1300
1	1,65	0,7	1,55
2	0,05	0,2	0,98
3	0,01	0,2	0,98

1) Process time in hours; 2) free calcium oxide (in %) at temperatures in degrees.

Calcium titanates of various compositions have been described in the literature. In the reaction of TiO_2 with $CaCO_3$, calcium metatitanate forms directly after dissociation of the carbonate, and only at temperatures above 1300-1350° with an excess of calcium oxide does tricalcium dititanate make its appearance [562]. According to Cocco*, we may also observe the formation of a titanate of the composition

TABLE 49

Binding of Calcium Oxide in its Reaction With TiO$_2$ in Mixtures of Various Molar Compositions

1 Температура в град.	2 Связанная CaO в пересчете на 1 моль TiO$_2$					
	4CaCO$_3$+TiO$_2$	3 CaCO$_3$+TiO$_2$	2CaCO$_3$+TiO$_2$	3 CaCO$_3$+2TiO$_2$	CaCO$_3$+TiO$_2$	3 CaCO$_3$+2TiO$_2$
900	0,98	0,97	0,82	0,76	0,51	0,47
1000	1,03	1,03	0,86	0,87	0,61	0,59
1100	1,07	1,06	1,1	1	0,99	0,66
1200	1,09	1,08	1,11	1	1	0,66
1300	1,40	1,16	1,13	1,09	1	0,66
1400 3	1,18	1,48	1,17	1,43	1	0,66
~3100 (ацетиленовое пламя)	1,61	1,57	1,58	—	—	—

1) Temperature in degrees; 2) bound CaO converted to 1 mole of TiO$_2$; 3) acetylene flame.

3CaO·TiO$_2$ at temperatures above 1480°. Yershov [564] showed that at temperatures below 1300°, CaTiO$_3$ (perovskite) is the least basic compound in the CaO-TiO$_2$ system. The process of CaO binding in the formation of CaTiO$_3$ is characterized after [564] by the data of Table 48 [564].

The results of a study made by Parga-Pondal' [565], which characterized the degree of binding of calcium oxide in its reaction with TiO$_2$ in mixtures of various compositions (Table 49) confirm the conclusions of Yershov in large measure.

Khedval and Anderson [566] established that at temperatures from 900 to 1200°, CaTiO$_3$ forms from anatase at a higher rate than from rutile. However, when the rutile (in the form of a solid solution) contains a few percent of ferric oxide, the rate of formation of CaTiO$_3$ from it is higher than the rate from pure anatase.

Calcium titanates (which are for the most part more basic than CaTiO$_3$) show viscous properties on reaction with water. They were studied in detail by Yershov.

Apart from those noted above, reactions in crystalline mixtures

have been used to prepare many other titanates — Na_2TiO_3, $ZnTiO_3$, $CdTiO_3$, $PbTiO_3$, and so forth (see, for example, [567, 568]). However, titanates of group II of D.I. Mendeleyev's periodic system have at the present time acquired the greatest practical importance, chiefly because of their special dielectric properties (which were studied in the work of Vul, Smolenskiy and others).

Pines and Kushta, who studied reactions in crystalline mixtures belonging to the $MgO-Cr_2O_3-TiO_2$ system, established by x-ray means that a compound $Cr_2O_3 \cdot 2TiO_2$ apparently forms in the $TiO_2-Cr_2O_3$ system. Only solid solutions of the spinelide type were detected in ternary mixtures (which contained a large quantity of magnesium oxide) after roasting at a temperature of 1650°.

The orthostannate Mg_2SnO_4, which possesses the spinel structure $(a_0 = 8.63$ A) forms in the $MgO-SnO_2$ system. Formation of this compound in a solid mixture was studied in detail by Berezhnoy [1]. The data that he obtained (see Fig. 138) indicate that this process takes place at a significant rate at temperatures above 1000°. According to Berezhnoy, the melting point of Mg_2SnO_4 exceeds 1950°.

As indicated by the investigations of Tanaka [569] and others [570], two compounds form in the $CaO-SnO_2$ system — the metastannate $CaO \cdot SnO_2$, which crystallizes in the rhombic system with elementary-cell parameters a = 3.93, b = 3.99 and c = 3.87 A, and the ortho-stannate $2CaO \cdot SnO_2$.

In a dry oxygen medium, the reaction between the initial oxides takes place at a noticeable rate at 900°. Its primary product at this temperature and higher temperatures is $CaO \cdot SnO_2$, which, given a sufficient quantity of calcium oxide in the reaction mixture, reacts further with it to form $2CaO \cdot SnO_2$ (Fig. 139). The reaction rate under the conditions studied is determined by the diffusion rate of the

starting reagents through the layer of product. The mechanism and
kinetics of the process are analogous to those prevailing in reactions
of MgO with TiO_2 and MgO with SnO_2, although the activation energy of
the CaO + SnO_2 reaction is somewhat smaller than that of MgO + SnO_2
[569].

The formation of alkaline-earth zirconates, which are of interest
for the production of refractory and electroceramic materials, has re-
cently been studied by numerous authors [444, 451, 453, 571 and others].

It has been established that the rate of the zirconate-formation
process in $RO-ZrO_2$ systems rises with increasing basicity of the
RO-type oxide.

The formation of only solid solutions in the ZrO_2 region with
limited solubility of the MgO has been established in the $MgO-ZrO_2$
system for temperatures up to $1700°$; here, the excess quantity of
magnesium oxide remains in the form of periclase according to x-ray
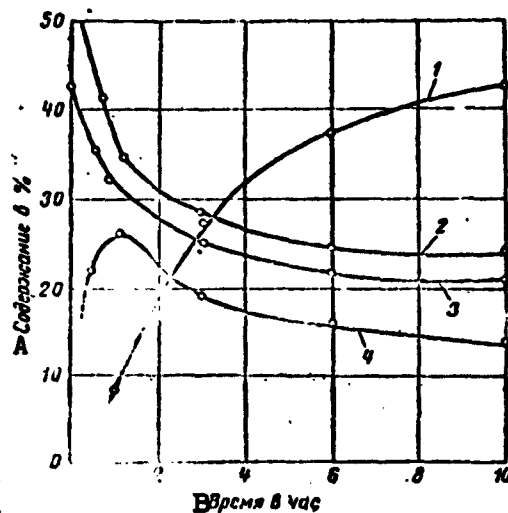and chemical analysis [444, 453].

Fig. 139. Reaction of calcium oxide with
stannic oxide. Kinetics of process with
CaO:SnO_2 = 2 and t = $1100°$. 1) 2CaOSnO_2;
2) SnO_2; 3) CaO; 4) CaOSnO_2. A) Content
in %; B) time in hours.

- 450 -

In contrast to the above, the zirconates $CaZrO_3$ and $BaZrO_3$ form in the $CaO-ZrO_2$ and $BaO-ZrO_2$ systems. The calcium zirconate is formed at a marked rate when $CaCO_3$ reacts with ZrO_2 at $600°$ and higher, and at temperatures of $900-1000°$ and above in the case of reaction of CaO with ZrO_2. Formation of barium zirconate may be noted at temperatures from 1100 to $1200°$ [453]. As for solid solutions, their formation has been established for the $CaO-ZrO_2$ system by Reference [453], while it has not been confirmed in the $BaO-ZrO_2$ system.

It should be noted that the rate of the zirconate-formation reaction at various temperatures is of great interest. For this reason, and in connection with a remark made earlier (page 390), it would be helpful to study it on pure zirconium dioxide, which might be produced by the method described in Reference [443].

As was established long ago by Tammann [211], divanadium pentoxide reacts with MgO and CaO at temperatures as low as $500-600°$.

According to Yander [572], the reaction may be noted in a mixture of MgO with V_2O_5 at a temperature as low as $450°$. In this system, the lines of the reaction product appear on the x-ray patterns when the mixtures are roasted to $530°$ and above. The reaction goes to completion in six hours at a temperature of $650°$. At relatively low temperatures (below $600°$), we observe reactions in mixtures of magnesium oxide or calcium oxide with MoO_3, WO_3 and UO_3. Substitution reactions accompanied by formation of the same products take place at high rates under the same conditions, e.g., reactions in mixtures of MgO with $ZnMoO_4$, $ZnWO_4$, $CdWO_4$, $MnWO_4$, and so forth.

The group of reactions considered briefly in this section is a very extensive one. New information concerning them and the properties and applications of their products in various branches of engineering are appearing almost every day. For this reason, we can only indicate

the necessity of systematic generalization of information on them that has come to light in publications of the most diverse kinds, some of which have been directed at very narrow audiences.

§4. SILICATES

Reactions in crystalline mixtures that form silicate systems constitute one of the broadest regions of solid-state chemistry. Their scientific and practical significance in the production of glass, cements and refractory materials is a well-known fact.

These reactions, like the processes of spinelide formation in mixtures of solids, may be classified as reactions in systems with R_2O, RO, R_2O_3, RO_2 and other oxides.

Let us consider the most important of these reactions.

Systems With R_2O

These systems and, primarily, the reactions that they encompass between silica and sodium carbonate, potassium carbonate and sodium sulfate, present particularly great interest for the glass making and alumina industries. Numerous research studies have been devoted to them (see, for example, [231, 339, 343, 399, 573-576]).

On the basis of the endothermic effect that they noted on the heating curve of a soda-quartz mixture, Tammann and El'sen [573] concluded that these substances begin to interact at a temperature of 780°. Subsequently, Khouers and Terner [399] showed that in equimolar mixtures of soda and silica, almost 90% of the substances has reacted after 14 hours at a temperature as low as 650°, while the reaction has gone practically to completion after 50 hours. However, the start of the reaction can be observed at a temperature of about 400°. The authors studied the course taken by reactions in mixtures of silica with soda in the molar proportions 4, 3, 2 and 1. It was established here that the reaction rate between the reagents is higher the higher

the silica content in the mixture; the rate of the reaction in the fourth mixture was lowest. This observation is easily accounted for on the basis of diffusion conceived as the limiting stage of the process. Actually, the layer of products, which form in this case on the silica grains, is the thinner and, accordingly, offers less resistance to the reaction the higher the content of SiO_2 in the mixture.
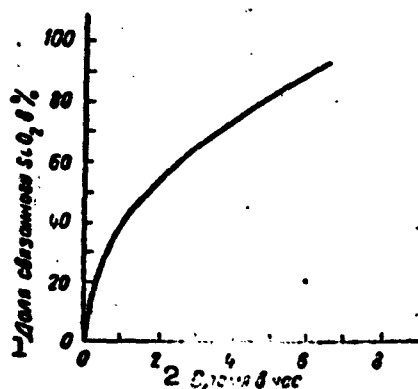

Fig. 140. Kinetics of reaction of soda with silica at temperature of 800° [339, 399]. 1) Fraction of bound SiO_2 in %; 2) time in hours.

Terner [339, 399] arrived at the conclusion that the reaction kinetics between soda and silica (Fig. 140) may be described by the monomolecular-reaction equation. The incorrectness of this idea was demonstrated later [231] (see pages 261, 282). According to Strokov [574], the reaction product in this case is sodium metasilicate Na_2SiO_3. Strokov even aserted that when mixtures of soda with silica are sintered, only this single compound forms, irrespective of the proportions of the reagents. This statement was subsequently refuted in the studies of Lileev [343], Toropov [119], Gibson and Uord [Ward] [575] and Ginstling [231]. It was established in these studies that given a sufficient content of sodium carbonate in the mixture (when $Na_2CO_3:SiO_2 \geq 2$), it reacts with silica to form sodium orthosilicate by the formula

$$2Na_2CO_3 + SiO_2 \to 2Na_2O \cdot SiO_2 + 2CO_2.$$
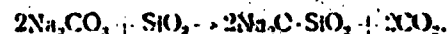
Budnikov and Matveyev [577] established the possibility of synthesizing sodium trisilicate $Na_2O \cdot 3SiO_2$ in mixtures of $Na_2CO_3 + 3SiO_2$ at temperatures of 700-750°, and investigated the properties of this

compound. Its refractive indices are $N_g = 1.5025$ and $N_p = 1.4965$, its specific gravity (the crystal silicate) is 2.9443, and its thermal-expansion coefficient is $165:10^{-7}$ [sic].

Potassium and lithium carbonates react with silica in the same way as soda [578].

In contrast to the above, sodium silicate reacts only very weakly with silicon dioxide even at high (above 1000°) temperatures. The reaction in the $Na_2SO_4 + SiO_2 + C$ system goes much more rapidly [579, 580].

Systems With RO

The formation of copper silicates by reactions in crystalline mixtures remains completely unstudied due to difficulties governed chiefly by the ease of the valence change in copper. It has been established only that cupric oxide reacts less rapidly with SiO_2 than zinc oxide and copper oxide [581].

Only 0.5% of the SiO_2 is bound by CuO as a result of a half-hour reaction at 650°. The lack of detailed data on reactions between the oxides of copper and silica is a serious obstacle to study of the physicochemical foundations of copper metallurgy. These reactions are also of considerable interest for the production of ceramic pigments.

Until comparatively recently, reactions in mixtures of BeO and SiO_2 and the diagram of state of the $BeO-SiO_2$ system, which is of great practical importance, had also been neglected.

To complicate matters further, the highly limited information on reactions in this system was contradictory. For example, Morgan and Gammel [582] failed to confirm Makhachki's observations [583] to the effect that phenacite $2BeO \cdot SiO_2$ forms at 1350° in a mixture of beryllium oxide with silicon dioxide in the absence of mineralizers. In Reference [582], phenacite was synthesized by heating a mixture of

BeO + SiO$_2$ (taken in 2:1 proportions) in the presence of 0.5-2% of willemite (Zn$_2$SiO$_4$) for 5 hours at a temperature of 1500°.

In 1950, Budnikov and Cherepanov [584] undertook a detailed investigation of the reactions of beryllium oxide with silicon dioxide in the presence of 2CaO·SiO$_2$, 2CdO·SiO$_2$ and MnO$_2$ as additives. Mixtures pressed under a pressure of 1000 kg/cm^2 were roasted in an atmosphere of air at temperatures of 1400, 1500 and 1600°. It was established by petrographic, x-ray and thermographic investigations that phenacite does not form at these temperatures in a mixture of pure BeO and SiO$_2$, nor in the presence of 2CaO·SiO$_2$ and 2CdO·SiO$_2$; manganese dioxide injected into the mixture in a quantity of 2% contributes to the formation of 2BeO·SiO$_2$ in it at 1500°; the phenacite synthesized decomposes in the temperature range from 1500 to 1600° (according to Morgan and Gammel [582] at a temperature of 1560°); the beryllium metasilicate noted in the literature is not detected under the conditions of the experiments.

Reactions in mixtures of silica with magnesium oxide and silica with calcium oxide, which are of exceptionally great importance and do not present any particular difficulties to research, have been studied in minute detail.

The first investigation of reactions between crystalline silica and magnesium oxide (not counting the recognized work of Cobb) was conducted over 40 years ago by Khedval [585]. It was established here that the reaction product is forsterite — magnesium orthosilicate, i.e., that the reaction follows the scheme

$$2MgO + SiO_2 \rightarrow 2MgO \cdot SiO_2.$$

Reactions in the MgO-SiO$_2$ system were subsequently studied in detail by Yander and Vurer [309], Berezhnoy [292], Bubenin [293], Kutateladze and Lutsenko [311, 400] and many other investigators.

According to Lutsenko [400], reaction between magnesium oxide and

silica with formation of small quantities of forsterite may be noted at a temperature of 900° after the process has been going for 1 hour.

Yander and Vurer [309] ran reactions in mixtures of MgO with SiO_2 with the molar proportions 2:1 and 1:3 and temperatures of 1100 and 1170°. Determining the composition of the roasting products by selective solution (using aqueous solutions of ammonium salts and dilute hydrochloric acid) and by x-ray analysis, the authors showed that the primary reaction product in these mixtures is Mg_2SiO_4, irrespective of their composition. This fact, which has a perfectly good thermodynamic basis [306] (Chapter 4, page 222) can be accounted for primarily by the simpler structure of the forsterite crystal lattice, which consists of isolated SiO_4^{4-} tetrahedra, while formation of magnesium metasilicate requires that these tetrahedra be connected in chains. The growth rate of the magnesium orthosilicate grain is therefore much higher than that of the metasilicate.

Figure 141 characterizes the difference between the formation rates of forsterite (Mg_2SiO_4) and magnesium metasilicate $(MgSiO_3)$.

Study of the kinetics of the reactions

$$MgSiO_3 + MgO \rightarrow Mg_2SiO_4$$
$$Mg_2SiO_4 + SiO_2 \rightarrow 2MgSiO_3$$
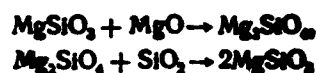
has shown [294] that the rate of the first is many times that of the second; this circumstance naturally contributes to the primary formation of forsterite.

It is interesting to note that at temperatures from 1100 to 1170°, the rate of formation of forsterite by the first of these reactions is [294] much higher than by the reaction

$$2MgO + SiO_2 \rightarrow Mg_2SiO_4$$

while at temperatures above 1200°, the rate of formation of forsterite from the oxides and from the metasilicate and oxide of magnesium are practically the same [293].
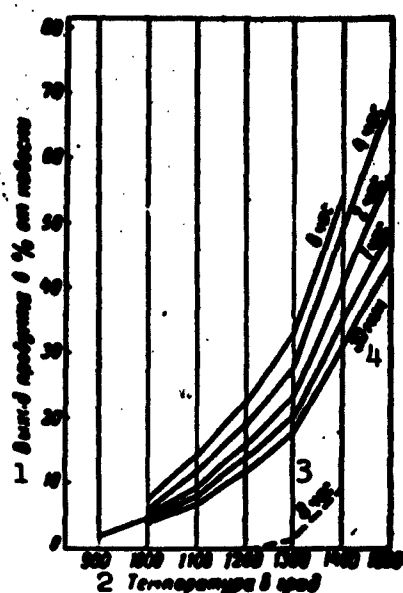
- 456 -

Fig. 141. Yield of Mg$_2$SiO$_4$
——— and MgSiO$_3$ ----- in
reaction of magnesium oxide
with silica in a mixture of
2MgO + SiO$_2$ as a function
of temperature [400]. 1)
Yield of product in % of
weight taken; 2) tempera-
ture in degrees; 3) hours;
4) minutes.

It was established by Berezhnoy
[292] that the rate of the forsterite-
preparation reaction depends little at
these temperatures on the form of the
initial mineral-silicate component.
Later investigations of Berezhnoy [385,
397] showed that this rate is also
practically independent of the form in
which the silica is used. Thus, the
yield of forsterite at a temperature of
1350° (in per cent of theory) runs as
follows: 58.6% in briquettes made from
magnesium oxide and quartz and 64.3%
from magnesium oxide and quartz glass.
For practical purposes, therefore (e.g.,
in refractory production), it is diffi-
cult to take advantage of the difference
between the formation rates of forster-
ite from different starting materials.

As was shown by Berezhnoy [292], the forsterite-forming reaction
goes practically to completion in two hours at a temperature of 1450°.
However, its crystals grow slowly, so that sintering of materials con-
taining Mg$_2$SiO$_4$ also proceeds with difficulty. This circumstance is,
as we know, a source of serious difficulty in the production of for-
sterite refractories.

Lutsenko [400] investigated the formation of magnesium silicates
in tableted mixtures of finely dispersed magnesium oxide and rock
crystal in the form of grains smaller than 0.06 mm with MgO:SiO$_2$ pro-
portions of 2, 10 and 0.1 (the first of which corresponds to the

- 457 -

forsterite refractory, the second to a forsterite-cemented magnesite refractory, and the third almost exactly to the composition of magnesium-cemented Dinas).

The roasting temperatures were 900, 1000, 1100, 1200, 1300, 1400 and 1500°; the process time at the 900° temperature was 1 hour, and it was varied from 30 minutes to 8 hours at $1000-1400^\circ$ and from 5 minutes to 4 hours at 1500°. As a result of chemical phase analysis and petrographic investigation of the roasting products, the sequence of reactions marked out earlier was confirmed for the $MgO-SiO_2$ system. Formation of forsterite was noted, as we stated above, at a temperature as low as 900°, and that of magnesium metasilicate was observed at 1300° in the first mixture and at 1200° in the third mixture.

The composition of the roasting products of forsterite mixtures depends heavily on the uniformity with which its components are mixed: an excess of silica at isolated points in the mixture results in formation of clinoenstatite by a secondary reaction. At temperatures between 1300 and 1500°, rapid progress of the reactions is assisted by development of quartz-regeneration and mineral-recrystallization processes. The results of Reference [400], some of which are presented in Figs. 141-143, enable us to draw inferences as to the kinetics of the silicate-forming process in this system over a broad range of temperatures, although it is difficult to agree fully with certain observations in Lutsenko's treatment.

The mass-transfer mechanism in the crystalline phases during the chemical reaction of magnesium oxide with silica reduces, according to Vagner [216], to counterdiffusion of magnesium and silicon ions (see §2 of Chapter 3). In view of the special importance of reactions in which magnesium silicates form in crystalline mixtures, it is appropriate to recall the processes that take place on heating of certain hydrated silicates. Among these, thanks to the work done by

Garal'dsen [586], the reactions that arise when serpentine is heated have been most thoroughly studied. They may be reduced basically to the following scheme:

$$H_4Mg_3Si_2O_9 \rightarrow 3MgO + 2SiO_2 + 2H_2O \rightarrow Mg_2SiO_4 + MgSiO_3$$
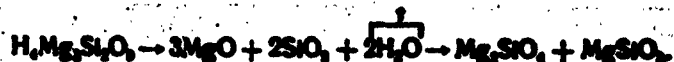
The contemporary conception of the course taken by this process may be represented schematically as in Fig. 144. The singularities of the serpentine crystal-lattice structure ("sheets" with interstitial hydroxyl groups) dictate progressive elimination of water as the temperature rises, with the formation of complex intermediate products in the process (which it has not yet been possible to isolate). After elimination of the greater part of the water, the serpentine is found to have decomposed into magnesium oxide and silica. On further heating of the mixture, these fine-dispersed oxides, which probably also have many crystal-structure defects, obviously undergo changes in accordance with the schemes described above (pages 386, 455) with formation of crystobalite and forsterite as the primary products. It is precisely these substances that figure as the crystalline products of decomposition of serpentine. Magnesium metasilicate appears only at high temperatures simultaneously with disappearance of the cristobalite.

Completely different processes take place in thermal decomposition of talc $3MgO \cdot 4SiO_2 \cdot H_2O$ [587-589]. The crystal lattice of talc contains elements that can easily be dismembered into chains of SiO_4^- tetrahedra, which form the basis of the lattice structure of the metasilicates of divalent elements. Consequently, talc does not decompose on heating into free oxides, but forms magnesium metasilicate and free silica directly. Eytel' [590], using an electron microscope, observed the formation of magnesium metasilicate and amorphous silica as primary products of thermal decomposition of $3MgO \cdot 4SiO_2 \cdot H_2O$. As in the case
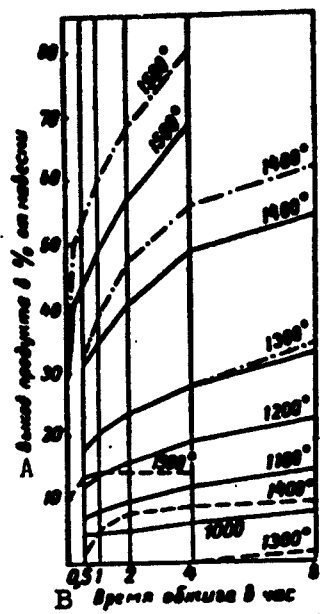
Fig. 142. Processes of
silicate formation in
a mixture of 2MgO +
SiO$_2$. ———— yield of
Mg$_2$SiO$_4$; — — — yield
of MgSiO$_3$; ·—·—·—
fraction of bound MgO
in %. A) Product yield
in % of weight taken;
B) roasting time in
hours.
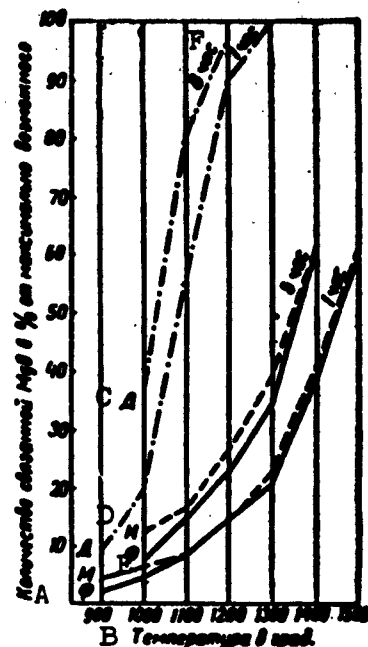
Fig. 143. Reaction of
MgO with SiO$_2$ in mixtures
of various compositions
at various temperatures.
— — — forsterite, first
mixture (2:1); ———— mag-
nesite-forsterite, second
mixture (10:1); ·—·—·—
third Dinas mixture (1:10).
A) Quantity of bound MgO in
% of maximum possible; B)
temperature in degrees; C)
Dinas; D) magnesite-forster-
ite; E) forsterite; F) 8
hours.

of decomposition of serpentine, complex intermediate products that
do not lend themselves to isolation form on thermal decomposition of
talc. Certain investigators (e.g., Tilo) find that in thermal decom-
position of talc, a special modification of magnesium silicate forms
at the beginning of the process; this is γ-MgSiO$_3$ or protoenstatite.
However, it has not yet been proven that this is not simply enstatite
or clinoenstatite with an imperfect crystal-lattice structure.

Passing over the inadequately studied and as yet highly debatable
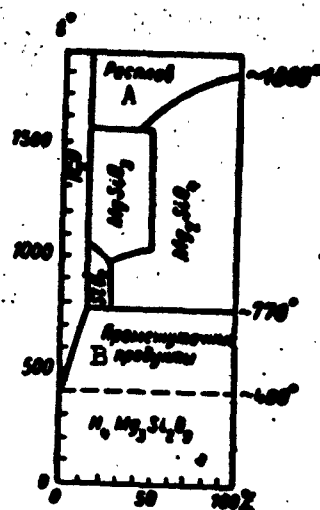
Fig. 144. Phase com-
position of serpen-
tine as a function of
temperature. A) Melt;
B) intermediate pro-
ducts.
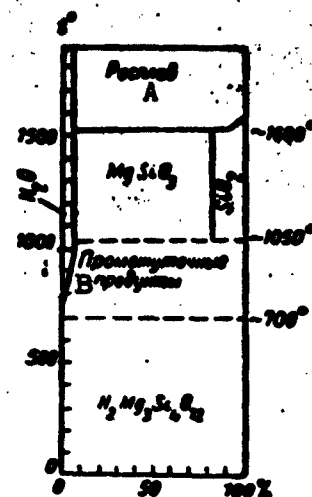
Fig. 145. Phase com-
position of talc as a
function of tempera-
ture. A) Melt; B) in-
termediate products.

details of the thermal-decomposition process of talc, we may repre-

sent the contemporary conceptions of the most important stages of

this process in the form of Fig. 145.

The thermal-decomposition processes of anthophyllite and sepialite

also proceed in much the same way as this process. The thermal-decom-

position processes of minerals of the humite group, which are important

from a theoretical standpoint, have been altogether neglected; this

represents a major gap in the physical chemistry of magnesium sili-

cates.

Information concerning reactions in the $MgO-SiO_2$ system, which

were described in very great detail above, form the scientific basis

for production of forsterite refractories and certain types of special-

purpose ceramics, and may also be used for production of special

bonding materials that contain magnesium silicates. Very little study

has as yet been devoted to the latter.

Four compounds are known in the CaO-SiO$_2$ system: CaO·SiO$_2$ (wollastonite), 3CaO·2SiO$_2$ (rankinite), 2CaO·SiO$_2$ (belite) and 3CaO·SiO$_2$ (alite). The reactions in which they form in crystalline mixtures, which constitute the physicochemical basis for production of Portland-cement clinker, have been studied in minute detail (see, for example, [118, 335, 344, 369, 371, 585, 591-594].

Extensive investigations of these reactions in the temperature range from 900 to 1550° were conducted by Nagai et al. [591], among others. According to their results, the primary reaction product at a temperature of 900° is Ca$_3$Si$_2$O$_7$ (rankinite), while Ca$_2$SiO$_4$ forms only at a temperature of 1200°. The observations of Strokov are in agreement with these data [574]. In contradiction to this, other investigators [118, 344] find that the primary reaction product of CaO and SiO$_2$ in crystalline mixtures is β-Ca$_2$SiO$_4$.

According to Yander [344], the course of reactions in a mixture of 2CaO + SiO$_2$ is represented schematically as in Fig. 46. The rather close similarity of these reactions to those in the MgO-SiO$_2$ system is characteristic. Yagich [595] observed the start of formation of the reaction products of calcium oxide with silica in their mixture at a temperature of 900°, using the emanation method. According to certain investigators [596], these oxides react with one another even at 550°. In the presence of CaF$_2$ or Fe$_2$O$_3$, the rate of reaction of CaO with SiO$_2$ increases considerably.

The investigations of Mamykin and Zlatkin [335], which were devoted to the kinetics of this reaction, confirmed the sequence of reactions in the CaO-SiO$_2$ system that we described earlier: their basic primary product is Ca$_2$SiO$_4$, with some Ca$_3$Si$_2$O$_7$. The silicate of composition CaSiO$_3$ forms only from these compounds (a more detailed investigation of the kinetics of silicate formation in this system was

undertaken in the studies of Toropov, Ginstling and Luginina [369, 371] and Chishmaru [373, 374]). Some results of these studies are described in Chapter 5.

Budnikov and Bobrovnik [597] established that at a temperature of 600°, the chief product formed in a mixture of $CaO + SiO_2$ (1:1) is Ca_2SiO_4 and, in smaller quantities, $Ca_3Si_2O_7$; at a temperature of 1000°, on the other hand, $CaSiO_3$ and $Ca_3Si_2O_7$ predominate in the reaction products, and β-Ca_2SiO_4 is present only in minor quantities. The authors confirmed the stepwise formation of the products in this system: Ca_2SiO_4 and $Ca_3Si_2O_7$ are unstable intermediate compounds, while the final product is $CaSiO_3$.

One compound of the system — tricalcium silicate Ca_3SiO_5 — cannot be produced by solid-phase reactions if we remain within the limits of the system's composition. Its rate of formation is exceedingly low and increases slightly in the presence of magnesium oxides, manganese oxide and chromic oxide [598, 599]. On prolonged exposure, tricalcium silicate decomposes in the solid phase at temperatures below 1200° and above 1900°.

It has been established [578, 585] by investigation of the influence exerted by the type of silica (precipitated silicic acid, quartz, cristobalite, quartz glass) upon the rate of its reaction with calcium oxide that there is a slight, if practically insignificant, rise in this rate in the case of unstable forms of SiO_2.

Preliminary heating of the quartz in the presence of certain gases has some effect on the intensity of its reaction with CaO. Here, according to Khedval [600], the reaction rate diminishes in the following series as a function of the composition of the medium in which the quartz has been previously heated: oxygen or sulfur dioxide, air, sulfur trioxide. However, the differences in the process rate are

practically insignificant in this case as well.

A comparative study made by Berezhnoy [397] on the reaction rates in synthesis of calcium and magnesium orthosilicates from the oxides has shown that the rate of Ca_2SiO_4 formation exceeds that for Mg_2SiO_4 at all temperatures. In the opinion of many investigators, this effect may be due to the higher reaction energy in the first reaction and the fact that the Ca^{++} ions have a higher mobility than the Mg^{++}.

Calcium orthosilicate exists in several modifications. Its polymorphic transformations, which were studied in detail only recently [601-606], are of very great importance. Correct understanding of these transformations and refinement of our conception of the crystal structure of the various modifications of bicalcium silicate have become possible as a result of application of improved x-ray research techniques, including high-temperature x-ray procedures. In view of the data of Bredig [601], Grin [602], Belyankin and Lapin [603], Val'kenburg and MacMurdy [604], Toropov et al. [605, 607], Midgeley [606] and certain other authors, the polymorphism of calcium orthosilicate may be characterized [316, 607] by the data of Table 50.

We have at our disposal information concerning the crystallization of the high-temperature α-$2CaO \cdot SiO_2$ in a simple hexagonal structure (and not in a complex monoclinic or triclinic structure, as was suggested earlier), chiefly as a result of References [602-604].

Bredig [601] was the first to refer to the existence of an intermediate α'-form of the orthosilicate, which corresponds structurally to β-K_2SO_4. The high speed of the $\alpha' \rightarrow \beta$- and $\alpha' \rightarrow \gamma$-transformations of $2CaO \cdot SiO_2$ prevents us from isolating the α'-form at high temperatures. However, its existence has been established by x-ray means: the x-ray diagram lines of bicalcium silicate, which has a temperature [sic] of 800-1000°, differ from those of α-, β- and γ-$2CaO \cdot SiO_2$

and resemble the lines of β-K_2SO_4.

In 1956, using direct traces of ionization x-ray diagrams at high temperatures for study of the polymorphic transformations of bi-

TABLE 50

Polymorphism of Bicalcium Silicate

1 Модификация	2 Кристаллическая система	3 Удельный вес	4 Показатели светопреломления		5 Температурная область устойчивости в град.		8 Аналогия модификации
			N_g	N_p	6 ниже	7 выше	
9 α-2CaO·SiO₂ (высокотемпературная форма)	10 Гексагональная	11 3,07 при 1500°	12 Не определены		2130	1420	α-2NaF·BeF₂
13 α'-2CaO·SiO₂ — бредигит (промежуточная устойчивая форма)	14 Ромбическая	3,31 при 700° 11	12 Не определены		1420	1230	α'-2NaF·BeF₂
15 β'-2CaO·SiO₂ — белит, фелит, ларнит (промежуточная неустойчивая форма)	16 Моноклиническая	3,28 при 20° 11	1,735	1,717	1230	650—900	β-2NaF·BeF₂
17 β-2CaO·SiO₂ (промежуточная неустойчивая форма)					650—900	450—760	.
18 γ-2CaO·SiO₂ (низкотемпературная форма)	14 Ромбическая	2,97 при 20° 11	1,654	1,642	450—760		2MgO·SiO₂ γ-2NaF·BeF₂

1) Modification; 2) crystalline system; 3) specific gravity; 4) refractive indices; 5) temperature region of stability in degrees; 6) below; 7) above; 8) analogy of modification; 9) α-$2CaO \cdot SiO_2$ (high-temperature form); 10) hexagonal; 11) at; 12) not determined; 13) α'-$2CaO \cdot SiO_2$, bredigite (intermediate stable form); 14) rhombic; 15) β'-$2CaO \cdot SiO_2$, belite, phelite, larnite (intermediate unstable form); 16) monoclinic; 17) β-$2CaO \cdot SiO_2$ (intermediate unstable form); 18) γ-$2CaO \cdot SiO_2$ (low-temperature form).

calcium silicate, Toropov et al. [607] established the existence of β'- and α'-modifications of this compound and obtained an x-ray diffraction characterization for them.

Because of the low symmetry of its lattice and the numerous polymorphic transformations of calcium orthosilicate, the structure of

belite β-2CaO·SiO$_2$ has thus far remained unstudied. It is assumed that belite crystallizes in the monoclinic system.

More detailed information on the modifications of bicalcium silicate may be found in the papers of Toropov [316, 607]. It is necessary to note that transitions of 2CaO·SiO$_2$ from one modification to another amount to a change in the position of the calcium ion in the crystal lattice. In the α- and β-forms of this silicate, the calcium ions are active coordination centers. Here we have maximum-density packing of the lattice structure elements; the molecular volume of the compound is less than the sum of the molar volumes of the oxides. In contrast to this, γ-Ca$_2$SiO$_4$, like Ca$_3$Si$_2$O$_7$ and CaSiO$_3$, shows a low packing density; the molecular volume of the compound is greater than the sum of the molecular volumes of the oxides.

Some of the polymorphic transformations described above, and particularly the β → γ transformation, are of practical interest: the β → γ transition is accompanied by a change of almost 10% in the volume of the silicate, and this may give rise to crumbling of the material (for example, cement clinker or dolomite) on cooling into a fine powder; moreover, the γ-form has practically no hydraulic properties.

In view of the above, prevention of certain transformations in this system and stabilization of the high-temperature forms (chiefly the α-form) of Ca$_2$SiO$_4$ is of great importance. The latter is based principally on the ability of calcium orthosilicate to form various types of solid solutions and on the properties of the latter.

By introducing minor amounts of certain additives that form stable solid solutions with the high-temperature hexagonal form of Ca$_2$SiO$_4$, we may manage to retard its transformation into the low-temperature rhombic form.

Al$_2$O$_3$, MgO, Fe$_2$O$_3$, TiO$_2$, Cr$_2$O$_3$, B$_2$O$_3$, P$_2$O$_5$ and many other oxides

may be used as the additives. Their solubilities in α-$2CaO \cdot SiO_2$ are, respectively, 0.5, 0.5, 1, 1, 2.5, 8, 1%, and so forth.

Toropov and Konovalov [605] established as long ago as 1938 that the high-temperature forms of Ca_2SiO_4 form solid solutions that show no tendency to undergo transformation to the γ-form with both $2BaO \cdot SiO_2$ and $2SrO \cdot SiO_2$. The authors studied these solutions in detail.

The action of all of the crystal-chemical additives listed above and others that reduce the temperature of conversion of Ca_2SiO_4 [by] up to 150° and more comes into evidence even when they are present in quantities equal to 0.5 mole-percent.

The so-called physical stabilization of Ca_2SiO_4 transformations by means of additives that do not form solid solutions with the silicate but break up its grains and weaken the influence of the internal stresses that arise in it in the polymorphic-transformation process is another known procedure. The influence of these additives becomes noticeable when they are present in contents of 2.5-3 mole-percent and higher.

In connection with the importance of problems of stabilizing α-Ca_2SiO_4 and preventing crumbling of products containing it, special research studies were devoted to these problems by Berezhnoy, Budnikov, Kukolev, Toropov and many other investigators. The results of these researches have been set forth in detail in the literature on bonding and refractory materials (see, for example, [296, 316]) and are therefore not considered here.

The reactions that take place in mixtures of CaO with SiO_2 are of very great importance for glassmaking, and for the production of Portland-cement clinker and dolomite refractories. The reactions are presently being exploited on the widest imaginable scale.

The formation of compounds in the SrO-SiO_2 system was studied in

Fig. 146. Reaction of SrO
with SiO$_2$ (1:1) at tempera-
ture of 920° [309]. 1)
Sr$_2$SiO$_4$; 2) SrSiO$_3$. A) De-
gree of conversion in %;
B) time in hours.

the work of Eskola [608], Yander et al.
[309 and others], Nertse [609], Keler
and Glushkova [610] and other authors.
The existence of three strontium sili-
cates has been established: SrSiO$_3$,
Sr$_2$SiO$_4$ and Sr$_3$SiO$_5$. The primary
product of the reaction in an oxide mix-
ture or a mixture of strontium carbon-
ate with silica is strontium orthosili-
cate (Fig. 146) irrespective of the
proportions between the original reagents.

According to Keler and Glushkova [610], the formation of this
product may be noted at a temperature of 900°. At 1800° and above, it
is converted into the metasilicate by the reaction

$$Sr_3SiO_5 + SiO_2 \rightarrow 2SrSiO_3$$

The rate of this process is relatively high, as a result of the appear-
ance of a liquid phase at a temperature of 1320°. In mixtures rich in
strontium carbonate, the tristrontium silicate also forms at a tempera-
ture of about 1100° together with the orthosilicate. Later, however,
it reacts intensively with the remaining silica to form Sr$_2$SiO$_4$:

$$2Sr_3SiO_5 + SiO_2 \rightarrow 3Sr_2SiO_4$$

as a result of which the product obtained at about 1400° is almost pure
orthosilicate [610].

Many papers have been devoted to barium silicates and their
preparation by reaction of the crystalline reagents. These include the
investigations of Eskola [608], Bouen [611], Yander et al. [309],
Krauze and Veyl' [612], Grube and Trukses [613] and many other
authors. Lately, a circumstantial investigation of the formation con-
ditions of barium silicates was undertaken by Keler and Glushkova

[314].

A detailed study of the $BaO-SiO_2$ system was conducted by Eskola [608] as long ago as 1922. The result of the work done in [309, 608, 611-613] and other studies was detection in the system of the compounds Ba_2SiO_4, $BaSiO_3$, $Ba_2Si_3O_8$ and $BaSi_2O_5$ as well as a continuous series of solid solutions between $BaSi_2O_5$ and $Ba_2Si_3O_8$. According to Trukses and Grube [613], barium metasilicate forms at first in the reaction of $BaCO_3$ with SiO_2. However, it was established in the highly meticulous research of Yander and Vurer [309] that irrespective of the proportions between the reagents in the initial mixture, the primary reaction product in this case is barium orthosilicate (see, for example, Fig. 49). The reaction proceeds rather rapidly even at temperatures just above 735°, while it can be noted only at about 1200° when $BaSO_4$ is heated with SiO_2.

Keler and Glushkova studied the reaction of BaO with SiO_2 with continuously rising temperature, as well as reactions in mixtures of $BaCO_3$ with SiO_2 at constant temperatures.

The initial mixtures were pressed at 460 kg/cm^2 and then heated while the temperature was being raised at a rate of $6-7^{\circ}/min$.

The authors established by complex thermal analysis [422, 423] (see Chapter 8), as well as chemical, x-ray structural and microscopic analyses, that barium orthosilicate forms in mixtures of barium carbonate with silica irrespective of the proportions between the initial components at temperatures of 800° and above. Beginning at about 700°, formation of minor quantities of barium metasilicate may be noted.

In mixtures that are rich in barium carbonate, tribarium silicate begins to form at about 1000° together with the orthosilicate.

With $SiO_2:BaCO_3$ proportions ≥ 1 in the initial mixture, formation of barium metasilicate is observed only when the temperature exceeds

1100°. The formation of $Ba_2Si_3O_8$ and $BaSi_2O_5$ was not confirmed by [314].

The authors synthesized Ba_3SiO_5 at a temperature of 1400° and determined its most important optical constants. It was established that the compound crystallizes in the hexagonal syngony with the elementary-cell parameters $a_0 = 15.62$ and $c_0 = 7.19$ [314].

The formation of willemite (Zn_2SiO_4) in the reaction of zinc oxide with silica and the remarkable fluorescent properties of this silicate were reported as long ago as 1929 by Pabst [614] and somewhat later by Karl' [615]. The first of these authors showed that the reaction in mixtures of ZnO with SiO_2 takes place at a noticeable rate at a temperature of 900°, with Zn_2SiO_4 alone forming irrespective of the mixture composition. At 980°, the yield of product is about 100% after 96 hours. When the above oxides are heated, the reaction between them passes through a number of stages. It can be detected at a temperature as low as 700°. The first lines of willemite in a pressed reaction mixture can be noted after it has been held at 800° for a few days (in the case of quartz as SiO_2) or at 950° (in the case of SiO_2 produced by hydrolysis of SiF_4).

It has been established by observation of dye sorption during the reaction process that the orthosilicate forms on the silica grains, with zinc oxide acting as the "coating" reagent [616].

The production of willemite by reaction in crystalline mixtures, which is limited to a relatively small scale, is nevertheless of considerable importance in connection with the use of this product as a brightly fluorescent material. Here, it is only necessary rigorously to regulate the sizes of the granules obtained and their impurity content.

The reaction of lead oxide with silica to form $PbSiO_3$ may be ob-

served at temperatures as low as 580° [211]; at relatively low temperatures (below 1000°), a liquid phase appears in the reaction mixture, leading to considerable intensification of the process. This reaction, which was recently studied in detail by Lindner [261] with the aid of radioactive indicators, takes place on heating of lead-oxide-containing glass and frit charges for glazing.

At the present time, very little study has as yet been devoted to reactions of MnO and FeO in crystalline mixtures with silicon dioxide, although they are of unquestioned interest. It is particularly important that the possibility of formation of ferrous-oxide metasilicate by reaction in a solid mixture be investigated; this has not yet been achieved in devitrification of glasses of the appropriate composition. In this case, we always observe formation of only iron orthosilicate — fayalite (Fe_2SiO_4), while, as we know, ferrous-oxide metasilicate — the so-called ferrosilite ($FeSiO_3$) — exists under natural conditions.

The occurrence of reactions in mixtures of NiO with SiO_2 and of Co_3O_4 with SiO_2 was demonstrated by Khedval [581].

Systems With R_2O_3
_____

Ferric oxide reacts neither with quartz nor with cristobalite [617]. However, formation of some unstable addition product that has not yet been isolated takes place in the Fe_2O_3-SiO_2 system at the instant at which the quartz undergoes transformation (at a temperature of 573°). When the quartz changes to cristobalite, the ferric oxide enters into solid solution in a small quantity; this is accompanied by an increase in the size of the cristobalite elementary cube from 6.99 to 7.02 A.

Chromic oxide (Cr_2O_3) does not react with crystalline silicon dioxide [205].

As we know, the Al_2O_3-SiO_2 system is extremely important, par-

ticularly for the production of ceramics. However, certain of its aspects still remain unclear in spite of the enormous number of research studies that have been devoted to it. Only recently has it become possible to eliminate a number of obscure points relating to it.
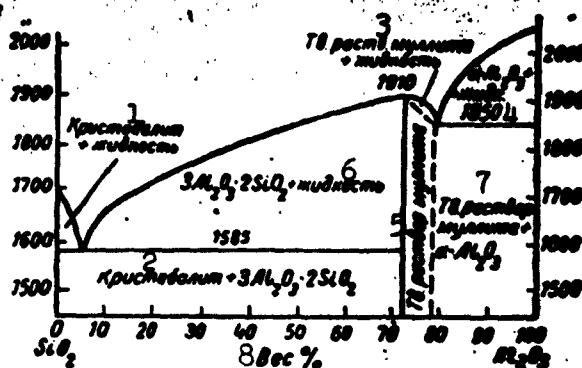
Fig. 147. Diagram of state of Al_2O_3-SiO_2 system. 1) Cristobalite + liquid; 2) cristobalite + ...; 3) solid solution of mullite + liquid; 4) α-Al_2O_3 + liquid; 5) solid solution of mullite; 6) ... + liquid; 7) solid solution of mullite + α-Al_2O_3; 8) % by weight.

The only chemical compound that forms in this system at high temperatures is mullite — $3Al_2O_3 \cdot 2SiO_2$. It crystallizes in the form of prismatic crystals of the rhombic syngony and has a specific gravity of 3 (according to other sources, 3.03). On the basis of data of Bouen and Greyg, who established the composition of mullite in 1924, it was assumed until quite recently that incongruent fusion of this compound takes place at a temperature of $1810°$ with decomposition into liquid and crystalline corundum. However, it was established by Toropov and Galakhov [618, 619] in 1951 that mullite actually melts without decomposition (the diagram of state of the Al_2O_3-SiO_2 system is shown in Fig. 147, according to Bouen and Greyg from 0 to 60% of Al_2O_3 and according to Toropov and Galakhov from 60 to 100% of Al_2O_3). The congruent melting of mullite in the Al_2O_3-SiO_2 system was then

confirmed by the x-ray, crystal-optical and thermal observations of Budnikov, Tresvyatskiy and Kushakovskiy [620].

For a long time, the relationship between minerals of the sillimanite group and mullite, understanding of which is necessary for a complete conception of the Al_2O_3-SiO_2 system, remained unclear. It became known as a result of the work done by Yakob [621] that crystalline kyanite and andalusite incorporate alkali in their crystal lattices, while the former also includes water. Transition of these minerals into mullite obviously involves elimination of these components, and this should take place in a certain temperature interval.

The circumstantial research done by Greyg [622] showed that the transition of kyanite and andalusite into mullite on heating actually takes place progressively, beginning from the grain surfaces. According-ing to Yakob and certain other authors, the ready transition of kyanite into mullite is accounted for by the presence of the water in its crystal lattice in addition to the alkali.
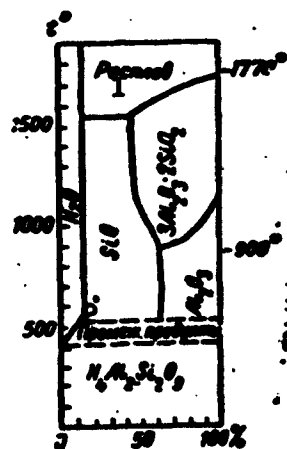
Fig. 148. Phase composition of kaolinite as a function of temperature. 1) Melt; 2) intermediate products.

It is highly probable that the sillimanite lattice also contains, in addition to the ions Al^{3+}, Si^{4+} and O^{2-}, certain other ions that are relatively firmly bound, the elimination of which is involved in the transition of sillimanite to mullite.

The reaction of mullite formation in crystalline mixtures, which has been the object of numerous investigations (see, for example, [238, 239, 623-626] and others), has nevertheless not been fully studied.

On heating, the aluminum hydrosilicates (kaolinite, pyrophyllite and others), which are

- 473 -

widely distributed in nature, give up water and are ultimately converted into mullite and cristobalite (Fig. 148).

The thermal-decomposition processes of these hydrosilicates are extremely complex and thus far remain completely unresearched. There are, among other things, various conceptions as to the nature of the dehydration products of kaolinite:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 + 2SiO_2 + \\ + 2H_2O,$$
$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + \\ + 2H_2O,$$
$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot SiO_2 + SiO_2 + 2H_2O,$$
$$4(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) \rightarrow 4Al_2O_3 \cdot 3SiO_2 + 5SiO_2 + 2H_2O,$$
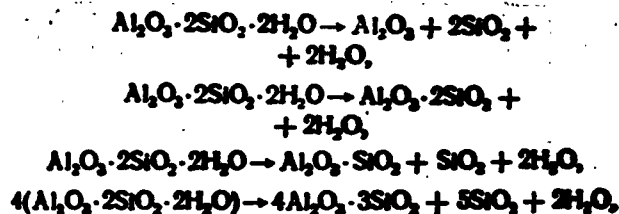
and, accordingly, as to the nature of the formation of mullite from these products:

$$3Al_2O_3 + 6SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2,$$
$$3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2.$$
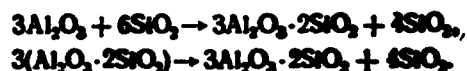
The most probable of the reactions listed above for the decomposition of kaolinite are the first two. As concerns the mullite-formation process, both of the reactions listed above and certain others are possible here.

The process of mullite formation may be observed at a temperature as low as $900°$, although its rate at even higher temperatures is relatively low; in practice, it does not go to completion when kaolinite is heated even after the melt has appeared ($1545°$). A certain quantity of alumina remains in the form of a glass (the growth of mullite grains proceeds very slowly in the absence of the so-called mineralizers).

Conducting the reaction of kaolin with alumina at temperatures of 1600, 1650 and $1670°$ with a reaction time of 2 hours, Budnikov established that the roasting products contained 76.2, 81.4 and 83.7% of mullite, respectively, corundum (6-10%) and a silica glass. Addi-

tives (2-4%) of $MgCl_2$, $MnCl_2$, P_2O_5 and B_2O_3 accelerated the crystallization process of the mullite.

Systems With RO_2 and Other Oxides

The dioxides of titanium and tin and the vanadium oxides V_2O_3 and V_2O_5 do not, as we know, react with silica. In contrast to this, ZrO_2 forms the compound $ZrSiO_4$, zircon, with silica. At high temperature, this silicate decomposes into ZrO_2 and SiO_2, with partial transition of the SiO_2 into the gaseous phase easily noted at temperatures above 1900°. Numerous research data on the "dissociation temperature" of zircon give figures in the temperature range from 1540 to 2000° and disagree widely with one another. Thus, for example, it is 2000° according to Reference [627], and 1500-1750° according to [628].

Such a significant difference in the figures obtained by different authors may be accounted for by the known arbitrariness of the very concept of dissociation temperature and the differences in the conditions (purification of the test materials, and so forth) and the methods of determination.

According to Zhirnova [629], the melting point of zircon is 2430°, while according to Kreydl [630], it lies between 2200 and 2500°.

The reaction

$$ZrO_2 + SiO_2 \rightarrow ZrSiO_4$$

can be noted at temperatures of 1460° and above. At the present time, this reaction, like the entire ZrO_2-SiO_2 system, which is of interest for refractory technology, has not as yet been thoroughly studied.

Even more neglected have been reactions in other binary systems including silica, such as P_2O_5-SiO_2, Bi_2O_3-SiO_2, and so forth.

Ternary and Multicomponent Systems

The most interesting among the ternary silicate systems is that formed by Na_2O, CaO and SiO_2, which is the basis of glassmaking. The

reactions taking place in it were studied by Tammann [573] and Terner et al. [631]. They established the formation, initially, of Na_2SiO_3 (at about 850°), followed by $CaSiO_3$ (about 1000°). Strokov [   ] showed that ternary compounds form in mixtures with all proportions of Na_2O, CaO and SiO_2 at temperatures above 1000°. The CaO-MgO-SiO₂ system has recently acquired great importance in the production of magnesium refractories. Taylor and Williams [632] made a series of experiments in the solid-mixture synthesis of all ternary compounds (with the exception of merwinite) encountered in this system. The authors demonstrated the possibility of producing akermanite and monticellite in mixtures of the oxides by heating them to temperatures of 600-1100°. Diopside was synthesized by Erenberg [633] somewhat earlier by holding a reaction mixture containing a small quantity of CaF_2 at a temperature of 620° for 525 hours. Merwinite was obtained in a solid mixture by Shtrassen [634] and Femister [635]. Thus was demonstrated the possibility of synthesizing all ternary compounds of this system in crystalline mixtures, and it remained only to study the course taken by the corresponding reactions. According to Taylor and Williams, the magnesium oxide may substitute calcium oxide in the silicates. This point of view was negated by Shtrassen [634] and Berezhnoy [397], who followed quantitatively (the former using powder diagrams and the latter by selective solution) the progress of reactions in which the magnesium oxide in the silicates was substituted by calcium oxide. These reactions take place at high speed and go to completion within 2 hours at temperatures from 1200 to 1300°. In studying various ways to form and decompose monticellite and merwinite, Berezhnoy [397] established that the preparation reactions of these compounds take place in stages.

Calcium orthosilicate, the formation rate of which is considerably

- 476 -

higher than that of Mg_2SiO_4 [and in the synthesis of monticellite even higher than that of $Ca_3Mg(SiO_4)_2$], is an intermediate product of the reaction. Only a comparatively small quantity of ternary compounds appears to form directly from the oxide, and then this happens only at temperatures of the order of 1300°. As a result of the low reaction rate in the formation of merwinite in a crystalline mixture, its synthesis is rendered difficult in practice, while monticellite, on the other hand, is produced relatively easily. The latter's rate of formation is relatively high when some of the magnesium oxide has been substituted by calcium oxide and low when the process corresponds to the equation

$$CaSiO_3 + MgO \rightarrow CaMgSiO_4.$$

Akermanite appears to form in the synthesis of monticellite from diopside as an intermediate product of the reaction.

Due to the fact that the product obtained in a synthesis of merwinite may retain a relatively large quantity of bicalcium silicate, which is an intermediate product of the reaction and sometimes causes decrepitation of specimens, the merwinite "cement" should be used with great caution in magnesium refractories.

Studying the changes undergone by thermolite on heating, Tilo [636] showed that a solid solution of magnesium metasilicate (clinoenstatite) in helenite and cristobalite forms from this mineral at a temperature of 1100°.

Krauze and Veyl' [612] set up separate experiments to study reactions in Na_2CO_3-$BaCO_3$-SiO_2 mixtures. However, their work is of the nature of preliminary research and the data obtained require improvement.
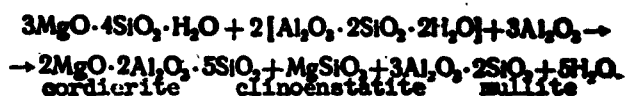
As yet, the reactions in the MgO-Al_2O_3-SiO_2 system have been the subject of little study. Investigation of the process in which the

only stable ternary compound of this system, cordierite $Mg_2Al_4Si_5O_{18}$, forms in this system would be of special interest, since it has direct importance for the technology of electrical ceramics and for certain other branches of engineering.

According to Bistrem [637], who investigated the behavior of an $MgO:Al_2O_3:SiO_2 = 20:40:40$ (percent by weight) mixture, the composition of which is near that of cordierite, observed first the formation of cristobalite, and then that of forsterite (Mg_2SiO_4) and spinel ($MgAl_2O_4$) in devitrification of a glass of this composition. Only later do cordierite and magnesium metasilicate (clinoenstatite and protoenstatite) form from these substances.

In this case, therefore, we have first the formation of binary and then that of ternary compounds.

Budnikov, Avetikov and Zvyagil'skiy [638] investigated the process in which cordierite forms in a mixture of talc with fireclay and alumina taken in proportions calculated stoichiometrically to produce $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$. The formation of this compound in such a mixture may take place according to the reaction

$$3MgO \cdot 4SiO_2 \cdot H_2O + 2[Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] + 3Al_2O_3 \rightarrow$$
$$\rightarrow \underset{\text{cordierite}}{2MgO \cdot 2Al_2O_3 \cdot 5SiO_2} + \underset{\text{clinoenstatite}}{MgSiO_3} + \underset{\text{mullite}}{3Al_2O_3 \cdot 2SiO_2} + 5H_2O$$

Roasting of the slurry obtained from the initial mixture was conducted at a final temperature of 1350°. It was established by x-ray investigation of the roasting products that when cordierite is produced from this raw material, clinoenstatite and mullite form simultaneously from the above starting material (by the reaction presented), as does spinel.

The $CaO-Al_2O_3-SiO_2$ system is exceptionally important for silicate technology, in that it encompasses the production not only of ceramics, but also of Portland-cement clinker, alumina, and so forth. There are

two principal ternary compounds in this system: helenite $Ca_2Al_2SiO_7$ and anorthite $CaAl_2Si_2O_8$. The first of these melts at 1590° and the second at 1550°. The possibility of their synthesis in a solid mixture has long been known, although its kinetics remained unstudied prior to the investigations of Yander and Petri [295]. These authors produced helenite and anorthite both from the oxides and from a mixture of $CaAl_2O_4 + CaSiO_3$ and mixtures of sillimanite with calcium carbonate or with $CaSiO_3$. In view of the difficulty of chemical separation of the materials in these cases, the authors employed the x-ray examination method. According to their data, the intermediate reaction products in the formation of helenite at a temperature of 1100° are the compounds $12CaO \cdot 7Al_2O_3$ (taken earlier for $5CaO \cdot 3Al_2O_3$) and $\beta\text{-}Ca_2SiO_4$; also present in the oxide mixture was $CaAl_2O_4$. After 1 hour and 45 minutes from the start of the experiment, calcium metasilicate also made its appearance. As the reaction advanced, the quantity of $CaAl_2O_4$ and $\beta\text{-}Ca_2SiO_4$ increased, while those of $12CaO \cdot 7Al_2O_3$ and $CaSiO_3$ diminished with the simultaneous appearance of helenite. After 7 hours 45 minutes, the reaction mixture contained a large quantity of helenite, as well as $CaAl_2O_4$ and $\beta\text{-}Ca_2SiO_4$. After heating for 185 hours, pure helenite was obtained.

Studying the formation of helenite by the reactions

$$CaSiO_3 + CaAl_2O_4 \rightarrow Ca_2Al_2SiO_7$$
$$12CaO \cdot 7Al_2O_3 + 6SiO_2 \rightarrow 6(Ca_2Al_2SiO_7) + Al_2O_3$$
$$\gamma\text{-}Ca_2SiO_4 + Al_2O_3 \rightarrow Ca_2Al_2SiO_7$$
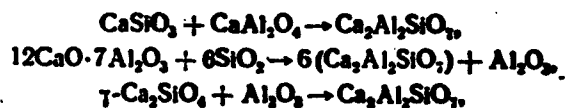
the authors arrived at the conclusion that the first of these takes place at a low rate at a temperature of 1100°: helenite can be detected only after 14 hours, and the reaction has not gone all the way to completion after 53 hours; no intermediate products form in this case.

According to Yander and Petri, the rate of the second reaction is

- 479 -

higher than that of the first (there is much helenite in the mixture after 1 hour 45 minutes, while the major part of the aluminate has reacted after 3 hours 45 minutes), and that of the third reaction is higher than that of the second (at 1100°, helenite lines are detected on the powder diagram after 15 minutes, and after 15 hours 45 minutes the reaction has gone almost to completion).

The rate at which sillimanite reacts with calcium carbonate is relatively high: at a temperature of 1100°, over 50% of the starting reagents have been converted into helenite after 7 hours 45 minutes:

$$Al_2SiO_5 + 2CaCO_3 \rightarrow Ca_2Al_2SiO_7 + 2CO_2.$$

The process in which helenite forms in a mixture of oxides takes place, according to Yander and Petri, in the following manner. The compounds $12CaO \cdot 7Al_2O_3$ and β-Ca_2SiO_4 form first. Then part of the aluminate reacts with SiO_2 and the orthosilicate with Al_2O_3 to yield the basic mass of the helenite. The $CaAl_2O_4$ and $CaSiO_3$ produced concurrently react slowly with one another to complete the formation of the helenite.

Anorthite may be synthesized from a mixture of kaolin with $CaCO_3$ and from mixtures of $CaCO_3$ with Al_2O_3 and SiO_2. The last reaction path, which lends itself more readily to inspection, was the one to which Yander and Petri devoted most of their study. After 15 minutes of heating at 1100°, the compounds $12CaO \cdot 7Al_2O_3$ and $CaSiO_3$, as well as small quantities of β-Ca_2SiO_4 and $CaAl_2O_4$ were identified in the reaction mixture. After 1 hour 45 minutes, diopside made its appearance in it, and after 7 hours 45 minutes the aluminate $12CaO \cdot 7Al_2O_3$ had vanished; here, the content of $CaSiO_3$ had diminished noticeably, while the content of β-Ca_2SiO_4 had increased. It is highly probable that anorthite was already present in the mixture but could not be identified because its lines are superimposed on others in the powder diagram.

After 15 hours 45 minutes had elapsed from the start of the experiment, the calcium metasilicate vanishes and the content of anorthite in the mixture increases. Even after 300 hours of exposure, however, diopside, cristobalite and β-Ca_2SiO_4 could still be detected in addition to anorthite in the reaction mixture.

TABLE 51

Sequence of Formation of Compounds in Synthesis of Diopside

*The sinter cake was obtained from a mixture of of $2CaCO_3$ + $Al(OH)_3$ + crystalline SiO_2.

1) Compound; 2) temperature in degrees; 3) lacking in sinter cake of composition*; 4) definitely distinguishable microscopically in sinter cake of composition*.

Study of the process of anorthite formation by the reactions

$$Ca_2Al_2SiO_7 + 2SiO_2 \rightarrow CaAl_2Si_2O_8 + CaSiO_3$$
$$Ca_2Al_2SiO_7 + Al_2O_3 + 3SiO_2 \rightarrow 2(CaAl_2Si_2O_8)$$
$$CaAl_2O_4 + 2SiO_2 \rightarrow CaAl_2Si_2O_8$$
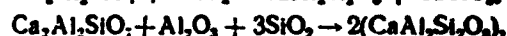
at temperatures from 1050 to 1100° led the authors to the conclusion that the first of these reactions proceeds at the highest rate: in it, anorthite may be detected after 1 hour 45 minutes. The formation of anorthite in the second and third reactions may be observed only after 3 hours 45 minutes. Here, the quantity of anorthite that has formed in the mixture is insignificant when the third reaction is run under these conditions even after 15 hours. When the temperature is raised to 1400°, the starting reagents are converted completely into

TABLE 52

Sequence of Compound Formation in Synthesis of Anorthite

1 Compound	2 Temperature in degrees			
	900	1000	1100	1200
12CaO·7Al₂O₃				
β-Ca₂SiO₄				
CaO·Al₂O₃				
CaSiO₃				
2CaO·Al₂O₃·SiO₂				
CaO·Al₂O₃·2SiO₂				

1) Compound; 2) temperature in degrees.

the anorthite after 10 hours.

Sillimanite undergoes virtually no reaction with calcium metasilicate. Thus, diopside forms as an intermediate reaction product in the synthesis of anorthite. However, according to Yander and Petri, anorthite forms directly in a mixture of kaolinite with $CaCO_3$.

According to Khedval [214], the reaction may be noted in such a mixture at temperatures of the order of 800°. Budnikov and Bobrovnik [597] showed that at a temperature of 600°, the process in which the calcium oxide is bound in a mixture with kaolinite has gone practically tc completion within 2 hours or less. The investigations of Strokov [574] showed that in reactions in mixtures of CaO with Al_2O_3 and SiO_2, the aluminate $(CaAl_2O_4)$ and silicates of calcium $(Ca_2SiO_4$ and more basic silicates) form as intermediate products.

A circumstantial investigation of the processes in which diopside and anorthite are formed by reactions in crystalline mixtures was made by Ginzberg and Lygina [294]. Conducting these processes in mixtures of various compositions at temperatures from 900 to 1200° and investigating the roasting products microscopically and by x-ray analysis, the authors arrived at the conclusion that the sequence of reactions leading to the formation of diopside and anorthite corresponds to

- 482 -

the description given above (see pages 211 and 213) and the data of Tables 51 and 52.

According to the authors, diopside is an intermediate product in all of the anorthite-synthesis reactions that they studied, including the synthesis of $CaO \cdot Al_2O_3 \cdot 2SiO_2$ in a mixture of kaolin with $CaCO_3$. Diopside itself forms from the high-temperature compounds $CaO \cdot Al_2O_3$ and $CaO \cdot SiO_2$, and not by reaction of $12CaO \cdot 7Al_2O_3$ with SiO_2 as had been suggested earlier. These data have thus made it possible to refine our conceptions considerably in regard to the sequence of reactions in the synthesis of diopside and anorthite.

TABLE 53

Parameters of Crystal Lattices of Diopside and $CaNi(SiO_3)_2$

1) Compound	a	b	c	β
$CaMg(SiO_3)_2$	9.71	8.89	5.24	74° 10'
$CaNi(SiO_3)_2$	9.67	8.88	5.25	74° 10'

1) Compound.

Reference [294] also indicates considerable intensification of these reactions in the presence of the "mineralizers" cryolite, fluorite and apatite.

Two ternary compounds are known in the $BaO-Al_2O_3-SiO_2$ system: $BaO \cdot Al_2O_3 \cdot 2SiO_2$ (celsian), the synthesis of which was studied as long ago as 1915 by Ginzberg, and an aluminosilicate of the composition $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$, which was first discovered and studied in 1954 by Toropov, Galakhov and Bondar'.

The above studies are important for several branches of chemical engineering.

Recently, G'yessing [639] obtained the nickel analog $CaNi(SiO_3)_2$

of diopside by reaction in a solid mixture. Study of this compound indicated that it is quite analogous to diopside as regards type of crystal lattice, while the parameters are very close to those of the latter compound (Table 53).

Among the more complex reactions in crystalline mixtures belonging to the silicate systems, the following are worthy of note: Yeger [640] proposed that beryllium oxide be produced from beryl by the reactions

$$Be_3Al_2Si_6O_{18} + 7CaO \rightarrow 6CaSiO_3 + CaAl_2O_4 + 3BeO$$
$$Be_3Al_2Si_6O_{18} + 13CaO \rightarrow 6Ca_2SiO_4 + CaAl_2O_4 + 3BeO$$
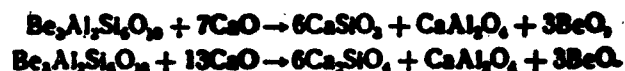
These reactions, which take place with noticeable speed at temperatures above 500°, are of great importance for the production of beryllium oxide — a valuable product used in the production of refractory and electrical-insulation materials.

Tsynkina [641] showed that zircon $ZrSiO_4$ reacts with magnesium oxide and calcium oxide. With a sufficient content of magnesium oxide in the mixture, the reaction corresponds to the scheme

$$8MgO + 3ZrSiO_4 \rightarrow 3Mg_2SiO_4 + Mg_2Zr_2O_9$$

According to Tsynkina, the bonding of magnesium oxide is characterized by Fig. 90 as a function of the maximum roasting temperature at which the reaction took place within 2 hours.

With a small content of magnesium oxide in the mixture, the reaction proceeds in accordance with the scheme

$$2MgO + ZrSiO_4 \rightarrow Mg_2SiO_4 + ZrO_2$$
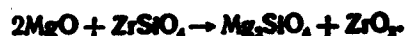
Zircon also reacts with alumina [642]:

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2ZrO_2$$

Both of these reaction types are highly important for the production of refractory materials.

The similar reactions of $ZrSiO_4$ with soda and lime (see, for example, [643]) are used to produce zirconium dioxide, which is used

in the production of refractory materials and as a substitute for cassiterite (SnO_2) for deadening of enamels [644].

Tammann [645] studied the reactions between MgO, CaO and BaO and aluminosilicates. Here, he arrived at the conclusion that magnesium oxide does not react with orthoclase, leucite, nepheline or hornblende at temperatures below 1000°, while CaO reacts with them at about 500° and BaO at 275°. At 1000°, calcium oxide reacts noticeably with willemite (Zn_2SiO_4). Barium oxide reacts with the silicates less intensively than CaO.

The data given here concerning the reaction temperatures of the substances were obtained by the heating-curve method described above and should be verified by means of modern methods for preparation of pure substances and investigation of reactions between them.

Berezhnoy [293, 397] showed that on heating in an oxidizing medium, mixtures of olivine with magnesium oxide and of forsterite with ferric oxide or chromic oxide undergo the following reactions:

$$(Mg, Fe)_2SiO_4 + MgO + O_2 \rightarrow Mg_2SiO_4 + MgFe_2O_4.$$
$$Mg_2SiO_4 + Fe_2O_3 \rightarrow MgSiO_3 + MgFe_2O_4,$$
$$Mg_2SiO_4 + Cr_2O_3 \rightarrow MgSiO_3 + MgCr_2O_4.$$
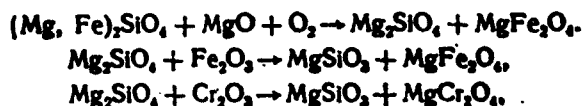
The progress of the second of these reactions was also confirmed by other investigators.

Berezhnoy [397] also showed that bicalcium ferrite reacts with forsterite and monticellite, forming bicalcium silicate and magnesioferrite.

Budnikov et al. [646-648] investigated reactions in mixtures of kaolin or clay with carbon (petroleum coke). The authors proceeded from the reaction in which mullite and carborundum form at temperatures from $1700-1800^{\circ}$:

$$3[Al_2O_3 \cdot 2SiO_2] + 12C \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiC + 8CO$$

and the formation of corundum and carborundum at temperatures from

1810 to 1830°:

$$Al_2O_3 \cdot 2SiO_2 + 6C \rightarrow Al_2O_3 + 2SiC + 4CO.$$

High-quality carborundum-mullite and corundum-carborundum refractory materials were obtained as a result of studies [646-648].

The above does not, of course, exhaust the information that has been published in the literature concerning the reactions of formation and decomposition of silicates in crystalline mixtures.

The material given here may be supplemented at the present time and will undoubtedly be the center of significant development in the next few years by the results of the numerous research studies being devoted to these reactions.

Manu-
script
Page
No.   [Footnotes]

391   Quite recently, Sazhin and Pepelyayeva [443] developed a
         method of obtaining pure zirconium dioxide containing less
         than 0.01% HfO_2, based on fractional recrystallization of
         potassium fluorozirconate from the system $K_2ZrF_6 + K_2HfF_6 + H_2O$.

398   M. J. Udy, Chronium, Vol. I and II, London, 1956.

399   M. I. Kochnev, P. V. Gel'd, O. A. Yesin, and N. N. Serebrenni-
         kov, Trudy Ural'sk. politekhn. in-ta [Transactions of the
         Urals Polytechnic Institute], 49, 163 (1954).

402   In certain cases, immiscibility or limited solubility has
         been observed in spinel mixtures [471]; this may possibly
         be explained by the low temperature at which reaction occurs.

422   The most recent circumstantial investigation of the proces-
         ses by which they are formed in the temperature range 800-
         1700° was made in Reference [515].

428      $BaAl_2O_4$ can be used as a binder for heat-resistant concrete
         (P. P. Budnikov, V. G. Savel'yev, Trudy MkhTI im. D. I. Mendel-
         eyeva [Transactions of the Moscow Institute of Chemical
         Technology imeni D. I. Mendeleyev], No. 27, 272, Gosstroyiz-
         dat [State Publishing House for Literature on Construction],
         Moscow, 1959.

445   For example, see W. Trzebiatowski et al., Experimentia

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	[Experimental Science], 6, 138 (1950); Roczniki Chem. [Annals of Chemistry], 28, I, 21 (1954); I.N. Belyayev, ZhPKh [Journal of Applied Chemistry], 26, 648 (1953).
447	A. Cocco, Rend. Semin. Fac. Sci. Univ. Cagliari [Reports of the Seminar of the Faculty of Sciences of the University of Cagliari], 25, No.3, 164 (1955).

Manu- script Page No.	[List of Transliterated Symbols]
403	пл = pl = plavleniye = melting

Chapter 10

CERTAIN FIELDS OF TECHNICAL APPLICATION OF
REACTIONS IN CRYSTALLINE MIXTURES

§1. CERAMICS AND REFRACTORIES

The technology of ceramic articles employs reactions in crystalline mixtures and the science that treats them in all of its branches: in the production of articles for gross structural ceramics, refractory materials, porcelain and faience, pigments, special electrical-engineering and other materials.

In the production of refractories and in the chemistry and technology of silicates, the polymorphic transformations of silica had hitherto been regarded as the simplest of solid-phase processes. Actually, however, these transformations, which represent an important factor in the manufacture of, for example, Dinas, are quite complex.

It has been established by research studies that the rate at which quartz is converted into tridymite and the extent of this transition, which determines the quality of Dinas articles and their behavior under operational conditions, depend on the grain size of the initial quartz, the quantity, structure and properties of the melt due to the presence of impurities in the quartz or a mineralizer in the original mixture, and on the temperature of the process and certain other factors (§1, Chapter 9). The dependence of the process rate and the extent of tridymitization of the quartz on the size of its grains, for example, is relatively complex in nature (page 389).

The accelerating effects of ferrous and ferric oxides and calcium

oxide on the tridymitization of quartz is a known factor. This effect is related to a considerable degree with the chemical reactions that take place in the presence of these oxides. For example, ferrous oxide (which is produced by reduction roasting of the initial mass) reacts with silica and lime to form relatively low-melting ferrosilicates. The appearance of eutectic melts of a definite structure creates conditions here that favor reconstruction of the silica lattice.

With calcium oxide hydrate or calcium carbonate present in the most insignificant quantities in the initial material (in practice, there is usually 1-3% of CaO in the production of refractory materials), it is necessary to reckon with the reactions that form calcium silicates (§4 of Chapter 9).

If the initial mass also contains a certain quantity of oxide impurities of aluminum, iron, titanium and other elements, the aluminates, aluminoferrites, aluminosilicates and titanates of calcium and similar compounds will accordingly appear when it is heated. Thus eutectics and subsequently melts of these eutectics, which promote transition of quartz to tridymite, are prepared. The exploitation of these effects in the production of Dinas and other products opens ways to deliberate regulation of their properties.

The process of mullite formation in roasting of kaolins and clays, which are the basic constituents of many ceramic masses, is of great importance for ceramic production.

As a result of the research done by Budnikov et al. [239], Iskyul', Krauze and other authors have recently formulated conceptions as to the mechanism of this process and made available information concerning its nature and intensity as a function of the nature of the starting raw material, temperature and certain other conditions (page 474). The behavior of mullite at high temperatures is of considerable interest for the technology of refractory materials: the properties

of high-alumina and other refractory materials are determined to a major degree by their mullite contents and the stability of the mullite on heating. Consequently, the processes of dissociation and the fusion and crystallization processes of mullite, and particularly the problem as to the manner in which it melts (incongruent or congruent fusion), which were studied in the papers of Toropov and Galakhov [619] and other authors, are of great practical importance.

Magnesium silicates form the most important constituent of certain ceramic products. These products include, for example, forsterite refractory materials, which consist for the most part of magnesium orthosilicate. The raw mass here contains olivine $MgO \cdot FeO \cdot SiO_2$ (or serpentine $3MgO \cdot 2SiO_2 \cdot 2H_2O$) and magnesite.

The content by weight of olivine (or serpentine) and magnesite is regulated in such a way that these materials will be converted as completely as possible during firing into magnesium orthosilicate (forsterite) and magnesium ferrite by the reactions

$$2(MgO \cdot FeO \cdot SiO_2) + 3MgCO_3 + \frac{1}{2}O_2 \rightarrow$$
$$\rightarrow 2(2MgO \cdot SiO_2) + MgFe_2O_4 + CO_2,$$
$$3MgO \cdot 2SiO_2 \cdot 2H_2O + MgCO_3 \rightarrow 2(2MgO \cdot SiO_2) + CO_2 + 2H_2O.$$
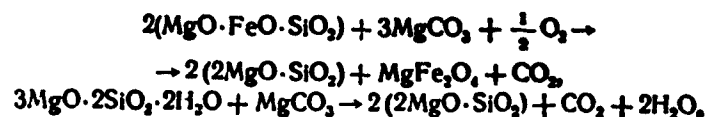
During firing, fayalite $2FeO \cdot SiO_2$, which is present in olivine (and serpentine), may combine with forsterite to form a solid solution that is detrimental to the quality of the forsterite brick. By using the formation reaction of magnesium ferrite, however, we may prevent the emergence of this solution. For this purpose, magnesite is introduced into the raw-material mass in a quantity sufficient to ensure not only the formation of forsterite, but also conversion of all the iron present in it into magnesium ferrite.

Silica is present in the raw mixtures for certain technically important refractory materials in quantities considerably smaller by comparison to the oxides of other metals. When such mixtures are fired,

- 489 -

the metallic oxides react with one another to form spinelides of the composition $MeO \cdot R_2O_3$ or $2MeO \cdot RO_2$. Ceramic technology also makes extensive use of the reactions of the spinelides themselves with crystalline oxides at high temperatures, which are accompanied by the formation of new compounds. To produce, for example, a chromite firebrick, the raw material selected is chromium ironstone, the basic substance in which is ferrochromite $FeCr_2O_4$. Together with ferrous oxide and chromic oxide, the ore usually also contains considerable quantities of magnesium oxide and aluminum oxide and approximately 3-6% of silicon dioxide. As a result of reactions with participation of MgO and Al_2O_3 (pages 409-418), fired chromite brick also contains, in addition to ferrochromite, magnesiochromite and aluminate spinel.

Despite the relatively small content of it in the initial raw material, the silicon dioxide may, in this case, be an essential factor in the firing process. It reacts with ferrous oxide to form the ferrosilicate $2FeO \cdot SiO_2$ (page 471), which serves as a cement for the chromite and spinel grains. A deficiency of SiO_2 results in a loss of refractory property and thermal stability in the chromite brick. Formation of the ferrosilicate in excessive quantities is naturally also undesirable. This may be avoided by binding the silicon dioxide with magnesium dioxide in forsterite by the reactions described earlier (see Chapter 9).

Thus, taking advantage of the known reactions in the system pertaining to the process under consideration enables us to regulate the composition and properties of chromite firebrick.

The approach to the production of chromomagnesite and other refractory materials is similar.

Above we gave a brief description of the part taken by reducing and oxidizing media in individual reactions in crystalline mixtures.

It will be appropriate here to touch upon the effect of water vapor on certain technological processes. It has been established that water vapor is capable not only of accelerating many such processes, but also in certain cases of exerting an essential influence on the composition and properties of the products obtained. For example, in the simultaneous presence of water in the firing atmosphere and reducing carbon in the raw-material mass, gaseous carbon monoxide and hydrogen form (by the reaction $C + H_2 \rightleftarrows CO + H_2$), and then take an active part in the chemical processes related to conversion of the mass into the product.

This principle is employed, for example, in production of the so-called "indigo" brick.

Reactions in crystalline mixtures have an important role in the production of lime pottery.

According to Rike and Pol'ker [649], the process in which the raw materials (consisting basically of kaolin, clay, quartz and calcium carbonate) are fired in the production of faience at a temperature of 900° is accompanied by formation of calcium aluminosilicate, which is readily soluble in acids, with only 1% of the CaO remaining unreacted. After firing at a temperature of 1000°, only traces of unreacted CaO can be detected; at 1100° and above, the molar composition of the acid-soluble part of the lime pottery corresponds to the synthesis of anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$, which is obviously formed on reaction of decomposition products of kaolinite and other minerals with calcium oxide.

High-refractory-oxide products constitute an important group of ceramic materials that are manufactured in part with the aid of crystalline-mixture reactions. These articles consist either of a single oxide, such as Al_2O_3, MgO, ZrO_2, ThO_2 (here, the processes that take

place on firing are restricted basically to sintering, recrystalliza-
tion, and polymorphic transformations), or of a combination of two or
three oxides (here, it is naturally possible for chemical reactions to
take place and for solid solutions to form). In the latter case, the
reactions in which high-refractory spinels such as $MgAl_2O_4$, $MgCr_2O_4$,
$FeCr_2O_4$ and the like are formed acquire special importance. Recently,
metals have sometimes also been added to the initial masses in the pro-
duction of these articles to improve their thermal conductivity. The
firing conditions (temperature, etc.) are adjusted in such a way as to
produce a dense, gas-impermeable product.

During the last few years, the processes in which such articles
are manufactured have been described in detail in the literature [413].

Extensive use is made of reactions in crystalline mixtures in the
manufacturing processes of insulating and other materials of high-fre-
quency engineering. Here it is necessary to deal with reactions between
MgO and SiO_2, Al_2O_3 and SiO_2 and many others.

The ceramics of electrical engineering incorporates three impor-
tant materials categories: insulating, semiconductor and magnetic.
All of these possess the same type of chemical bond — that of the ionic
crystal-lattice structure.

The first category includes:

a) ceramics for installation hardware and low-capacitance con-
densers (steatite, ultraporcelain, radioporcelain, celsian ceramics,
and corundum-mullite materials);

b) ceramics for high-frequency and low-frequency capacitors (ru-
tile, perovskite, titanium-zirconium, stannate, strontium-bismuth ti-
tanate);

c) ferroelectric and piezoelectric ceramics for low-frequency
capacitors, piezoelectric and nonlinear elements (solid solutions of

titanates, zirconates, stannates).

The second category is composed of ceramics for semiconductors, high-power radio-frequency resistors, high-temperature heater units, nonlinear elements and thermistors manufactured on the basis of copper- and cobalt-manganese inverse spinels and certain other compounds.

The third category embraces magnetically soft and magnetically hard ceramics (nickel-zinc, manganese-zinc, magnesium, barium and other ferrites). The most complete description of nonmetallic ferromagnetic materials and ferroelectrics was given by Smolenskiy.*

A classification of the crystalline phases of electrical-engineering ceramics according to Bogoroditskiy and Fridberg [650, 651] is represented in Table 54.

Other important crystalline phases in high-frequency ceramics are quartz, celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$), perovskite ($CaTiO_3$), zirconium titanate ($ZrTiO_4$), calcium stannate ($CaSnO_3$) and calcium zirconate ($CaZrO_3$).

All of these compounds and others named above belong to the $BaO-Al_2O_3-SiO_2$, $MgO-Al_2O_3-SiO_2$, $CaO-Al_2O_3-SiO_2$, $ZrO_2-Al_2O_3-SiO_2$, $BaO-ZrO_2-TiO_2$, $MgO-ZrO_2-TiO_2$, $CaO-ZrO_2-TiO_2$, $SrO-Bi_2O_3-TiO_2$, $CaO-SnO_2-TiO_2$, $CaO-SrO-BaO-TiO_2$ and $CaO-SrO-BaO-TiO_2$ systems.

The properties of ceramic materials manufactured on the basis of these compounds that are of greatest importance for radio engineering are their dielectric strength, dielectric losses, mechanical and sparkover strengths, coefficient of thermal expansion, Curie point, modulus of piezoelectric effect and certain others. Knowing these properties as functions of the composition and structure of the initial materials and the processing conditions applied to them (pressing; firing, and so forth), we may produce ceramic products of the required quality.

For example, in producing one of the most important materials of high-frequency technique — steatite — from talc, a natural hydrated magnesium silicate of the composition $3MgO \cdot 4SiO_2 \cdot H_2O$, we regulate the electrical properties of the product (and its dielectric-loss factor in particular) through the composition of the initial mixture. On firing, the talc is first converted into protoenstatite and then into clinoenstatite. Cristobalite forms from the excess silica. To bind it, barium carbonate [215], which reacts with SiO_2 at temperatures as low as $600-700°$ [612], is added to certain steatites.

The recipe for a steatite ceramic and the process conditions are selected such as to exclude the possibility of polymorphic transformations of the basic crystalline phase of the product, magnesium silicate, under operational conditions and during storage of the articles. Zirconium dioxide is introduced into certain steatites as a mineralizer to promote formation of fine-crystalline material and, accordingly, contribute to increased mechanical strength [651]. A steatite (grade S-55) whose recipe includes a clinoenstatite sinter prepared from talc and magnesite in proportions calculated to bind all of the silica liberated in the decomposition process of the talc when it is heated possesses particularly high mechanical strength. The raw-material mass for this steatite also contains raw talc corresponding to the quantity of magnesite, a small quantity of clay and zinc oxide as a mineralizer.

To produce electrical-engineering products with extremely low coefficients of thermal expansion and high thermal-shock resistance, talc and kaolin or clay, and sometimes certain other materials, are introduced into the raw-material mixture in such weight proportions that cordierite $MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ will be formed during firing as a result of chemical reactions in the mixture (see page 478).

TABLE 54

Classification of Crystalline Phases in Electrical-Engineering Ceramics

1 Тип кристаллической фазы	2 Характер упаковки ионов, особенности химической связи	3 Минералы (примеры)	4 Химическая формула	5 Характер электропроводности	6 Показатель преломления	7 Тангенс угла диэлектрических потерь при радиочастотах	8 Удельное объемное сопротивление, ом·см
9 Кристаллы-диэлектрики с малым коэффициентом преломления	10 Рыхлая структура (несоответствие условию плотнейшей упаковки, большие анионные числа при малой зарядности катионов)	Кордиерит 11, Берилл 12, Альбит 13	2MgO·2Al₂O₃·5SiO₂, Al₂O₃·..., Na₂O·Al₂O₃·6SiO₂	14 Заметная (собственная или примесная)	1,537 1,56 1,531	До 0,01	10⁸—10¹⁴
15 Кристаллы-диэлектрики с промежуточным и средним коэффициентом преломления	16 Плотная упаковка, высокая энергия перехода катиона в состояние другой зарядности	18 Волластонит, 19 Клиноэнстатит, 20 Муллит	CaSiO₃, MgSiO₃, 3Al₂O₃·2SiO₂		1,631 1,655 1,648	<0,0005	~10¹⁴
	17 Плотная упаковка, незначительная энергия перехода катиона в состояние другой зарядности	21 Периклаз, 22 Шпинель, 23 Корунд	MgO, MgAl₂O₄, Al₂O₃	24 Заметная или высокая электронная	1,736 1,718 1,768	<0,0003	~10¹⁴
	1 Плотная упаковка...	Рутил 25, Тип перовскита 26	TiO₂, Nb₂O₅, ZnO		2,616 2,8 2,004	27 Резко зависит от примесей	10⁶—10¹⁴
28 Кристаллы-сегнетоэлектрики	29 Доменная структура, 30 То же	30 Тип перовскита, 31 То же, 32 Тип пирохлора	BaTiO₃, KTaO₃, Cd₂Nb₂O₇	33 Электронная	2,4 — —	>0,01	10¹³ 10¹⁴

1) Type of crystalline phase; 2) nature of ionic packing; characteristics of chemical bond; 3) mineral; 4) chemical formula; 5) type of conductivity; 6) refractive index; 7) dielectric loss tangent at radiofrequencies; 8) volume resistivity in ohms·cm; 9) dielectric crystals with low refractive index; 10) loose structure (nonconformity to closest-packing condition, large anion numbers with low cation charge); 11) cordierite; 12) beryl; 13) albite; 14) marked ionic conductivity (intrinsic or "impurity"); 15) dielectric crystals with intermediate and medium refractive index; 16) close packing, large energy of transition of cation into other charged state; 17) close packing, insignificant energy of transition of cation into other charge state; 18) wollastonite; 19) clinoenstatite; 20) mullite; 21) periclase; 22) spinel; 23) corundum; 24) marked or high electronic conductivity; 25) rutile; 26) wuertzite type; 27) depends heavily on impurities; 28) ferroelectric crystals; 29) domain structure; 30) perovskite type; 31) same; 32) pyrochlore type; 33) electronic.

Ceramic capacitors based on titanium dioxide are being used successfully in contemporary high-frequency engineering. The initial compounds used in the production of such capacitors also contain oxides of other metals for the purpose of forming titanates during the firing process; the properties of the condenser ceramic — its dielectric constants, dielectric loss factor and others — are regulated by varying the proportions between these oxides.

Magnesium orthotitanate and barium metatitanate are important titanates for high-frequency technique. However, oxides of other metals are also used together with the magnesium and barium oxides or carbonates to produce the condenser raw materials.

Naturally, information on the sequence of the thermal and volume effects in titanate-synthesis reactions that has been obtained by researchers [562] and others) is of essential interest in selecting efficient systems for synthesis of these compounds under industrial conditions.

We discussed above the processes in which spinelides are produced in the manufacture of refractory materials. These compounds and their formation reactions are also important in the manufacture of high-frequency ceramics. In this case, the spinels have a dual importance: as materials with high resistivity and as nonmetallic ferromagnetics.

The formation of ferrites, which are ferromagnetic materials possessing very low conductivities, has acquired particular importance in connection with the development of high- and ultrahigh-frequency technique. These compounds, which have the general formula $Me_xFe_y^{3+}O_z$ (where Me is a uni-, di- or trivalent metal), and metaferrites of the composition $Me^{2+}O \cdot Fe_2O_3$ in particular, which are used widely in radar, electroacoustics, contemporary computer technique, etc., are also produced by reactions in mixtures of crystalline reagents (oxides).

It is essential to note that there are considerable differences between the properties of different spinelides. Thus, the resistivity of the "inverse spinel" Fe_3O_4 is several hundred $ohms^{-1} cm^{-1}$, while that of normal aluminum-magnesium spinel is 10^- [superscript illegible] $ohms^{-1} cm^{-1}$. Zinc and cadmium ferrites, which have the structure of normal spinel, possess paramagnetic properties, while certain other ferrites (of the "inverse"-spinel type) show ferromagnetic properties. Only by calculating the composition of the raw-material masses carefully and by specifying the firing conditions for them strictly in order to produce specific compounds and solid solutions will it be possible to regulate the properties of the ceramic products with an accuracy sufficient for high-frequency technique. Reactions in mixtures of crystalline oxides have been used for many centuries to produce ceramic pigments. Like other fields of application of the so-called solid-phase reactions, this field has for centuries been in the province of the arts, but not of science. Only comparatively recently were systematic investigations undertaken into the relationship between the crystal structure and properties of the pigments, together with penetrating study of the various processes in which they are produced.

The manufacture of ceramic pigments is based on the formation of silicates, aluminates, aluminosilicates and similar compounds, as well as various solid solutions and mixtures between them, to which various colors are imparted. Various oxides are generally added to white and colorless masses as coloring agents. For example, ferric oxide is used to produce yellow, red and brown colors, brown colors are also produced by manganese oxide, blue by cobalt oxide, green by chromic oxide, etc. (compounds of antimony, nickel, copper, uranium and other metals are also used to color enamels).*

It is far from always an easy task to produce stable pigments

that do not change color on exposure to high temperature, moisture, air, carbon dioxide, and so forth. It is known that firing certain substances in media of various compositions results in the formation of products having various corresponding colors. In particular, addition of red clay with a high ferric-oxide content (or simply addition of ferric oxide) to a white or yellow clay to color it red frequently does not lead to the desired results: even with low firing temperatures, the mass turns gray or violet. In these cases, only the solid solution of ferric oxide in aluminum oxide retains its red coloration even in high-temperature firing (the circumstance taken advantage of in practice).

It would be possible to cite many examples in which ceramic pigments are produced by reaction in mixtures of crystalline reagents.

Even in his work of 1912-1915 Khedval succeeded in synthesizing Rinmann's green $CoZnO_2$ from white zinc oxide and black cobalt oxide and "matte blue," cobalt aluminate, from the white Al_2O_3 and black CoO.

At the present time, cobalt ultramarine is produced by precisely the same formation of aluminates — $CoAl_2O_4$, $CoAl_4O_7$, $CoAl_6O_{10}$ and others. It is true that in practice, we deal in this case not with a reaction between two or three pure oxides, but with complex systems in which SiO_2, Al_2O_3 and other oxides are chemically bound, e.g., in the form of kaolin, feldspar, and so forth.

The violet lower silicate of cobalt is produced by the reaction

$$2CoO + SiO_2 \rightarrow Co_2SiO_4.$$

The metasilicate $CoSiO_3$ and the polysilicates $CoSi_2O_5$, $CoSi_3O_7$ of cobalt and other substances are produced in a similar manner.

Such are the nature and significance of reactions in mixtures of crystalline solids in ceramics technology.

These reactions lie at the foundation of modern methods for pro-

ducing ceramic products and refractory materials for the construction of the most important apparatus and equipment of the metallurgical, structural, chemical-engineering, electrical-engineering and radio-engineering industries. These reactions serve as a means for producing porcelain, faience, ceramic pigments and many other ceramic materials as products used in almost all branches of the national economy.

§2. CEMENTS

The chemistry and technology of cements make up one of the most important trends in the technical application of solid-state reactions. Various types of cementing materials, which form mortars and cements with various technical properties on reaction with water are produced on large industrial scales on the basis of these reactions.

As regards their phase composition, cements are various combinations, chiefly of basic silicates, aluminates and aluminoferrites of calcium that are formed as a result of decomposition and reaction of the components of the corresponding raw materials at high temperatures. Depending on the function of the cement clinker, the raw-material mixtures may include, in various proportions, limestone rock, marls, argillaceous rock, furnace slag, bauxite and other materials.

The chief minerals in Portland cement clinker are $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$; here, according to Okorokov [652], the sum of the first two components normally represents from 75 to 80% of the gross phase composition of the clinker. Together with these minerals, the composition of Portland cement may include $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$, $2CaO \cdot Fe_2O_3$, $5CaO \cdot 3Al_2O_3$ and, in minor quantities, certain other compounds.

The basic components of aluminous cement are the aluminates $5CaO \cdot Al_2O_3$, $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$. In addition, an aluminous cement may contain helenite, $2CaO \cdot Al_2O_3 \cdot 2SiO_2$, akermanite $2CaO \cdot MgO \cdot 2SiO_2$, as

well as dicalcium silicate, calcium ferrites, magnesium spinel and certain other substances, both in "pure form" and in the form of solid solutions.

The chemical and physicochemical reactions that lead to the formation of the various cementing substances belong primarily within the $CaO-Al_2O_3-Fe_2O_3-SiO_2$, $CaO-MgO-SiO_2$, $MgO-Al_2O_3-SiO_2$, $R_2O-CaO-Al_2O_3$, $R_2O-CaO-SiO_2$, $R_2O-CaO-Al_2O_3-Fe_2O_3$ systems, followed by systems containing CaF_2, P_2O_5, TiO_2, SO_3, Cr_2O_3 and certain other compounds (here, no less than 90-95% of the cement-clinker composition is formed by compounds and solid solutions of the first system in the majority of cases).

This makes clear the importance of study of reactions in these systems for the technology of bonding substances.

The chemistry of cements and, in particular, the processes in which the cement-clinker minerals form have been studied in detail in the monographs of Bog [653], Kyul' [654], Li [655], Toropov [316] and Yung [656]. The formation reactions of the silicates, ferrites and aluminates of alkali and alkaline-earth metals were described above in Chapter 9. Here, therefore, we may limit ourselves simply to a general characterization of the conditions and processes of cement-clinker mineral formation and a description of the results obtained in certain more recent studies pertaining to it.

Under practical cement-production conditions, the initial mixture is gradually heated in an annealing furnace from room temperature to $\sim 1450^\circ$. At about 1280° (or sometimes a lower temperature, depending or mixture composition), a liquid phase appears in the reaction mixture. Passing through the "cooling zone," the cement clinker has a temperature of about 1000° at the exit from the furnace.

The sequence of reactions in the formation of cement-clinker

minerals reduces in approximation to the following in cases where calcium is introduced into the mixture in the form of its carbonate.

When the mixture has reached a temperature of $600-800^\circ$, we may observe a certain amount of carbonate dissociation and very slow, practically negligible reactions between the calcium oxide on the one hand and the silica and sesquioxides on the other. The rate of these reactions rises noticeably with temperature, and intensive formation of calcium monoaluminate takes place in the temperature range from 800 to 1000°, so that when the mixture reaches 1000° all of the alumina has been bound in the form of $CaO \cdot Al_2O_3$. Here the quantity of the primary calcium silicate formation (the orthosilicate $2CaO \cdot SiO_2$) is still comparatively small. As the temperature rises progressively to 1200°, the calcium monoaluminate reacts with the unreacted lime to form $5CaO \cdot 3Al_2O_3$ and then $3CaO \cdot Al_2O_3$.

As was shown by Toropov and Dyuko [277], reaction of the calcium oxide with the ferric oxide begins at a temperature of about 900° with formation of bicalcium ferrite $2CaO \cdot Fe_2O_3$ as the primary product. At a temperature of 1200° and slightly above, intensive formation of bi-calcium silicate, which goes to completion in this stage of the process, and possibly of tetracalcium aluminoferrite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ take place.

As the temperature rises to $1280-1300^\circ$, completion of all reactions listed above takes place, although the excess of lime remains free.

Then the next stage of the process intervenes; this is sintering with participation of the liquid phase, which provides conditions for reaction between the bicalcium silicate and the lime leading to the formation of $3CaO \cdot SiO_2$.

In cases where gypsum or anhydrite is the source of calcium in

the reaction mixture (so that carbon will also be introduced in some form or another into the mixture), the cement-clinker formation process consists of three basic stages:

1) reduction of calcium sulfate by carbon to calcium sulfide;

2) reaction between the calcium sulfide and sulfate with formation of calcium oxide and sulfur dioxide;

3) reaction of the calcium oxide with the oxides of silicon, aluminum and iron to form silicates, ferrites, and aluminates of calcium and other minerals.

Each of these stages (which were studied in the work of Zavadskiy [318], Royak [320], Simanovskaya, Shpunt [657], the authors of the present monograph [317, 658] and certain other investigators) consists in turn of a number of physical and chemical phenomena; to a certain degree, they are illuminated in the references cited above. Certain stages overlap in time.

The problem of efficient design and deliberate control of the process in which a cement with specified properties is made (which are determined by the chemical and phase composition and physical structure of the cement clinker and by the properties of its vitreous phase) naturally requires rigorous control of the reactions discussed above.

Let us note in this connection that not all compounds that may be formed on firing of the reaction mixture in cement production possess adhesive properties. For example, the silicate of composition $3CaO \cdot 2SiO_2$ (rankinite), which may be produced in a certain quantity simultaneously with the $2CaO \cdot SiO_2$, and the calcium aluminosilicate of the composition $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite), which appears in the production of aluminous cement, are lacking in these properties. Naturally, the content of these compounds in the cement clinker should be reduced to a minimum.

The adhesive properties of certain other possible components in cement clinker, such as helenite $2CaO \cdot Al_2O_3 \cdot SiO_2$ and the γ-modification of calcium orthosilicate, depend on their structure and the hydration conditions. Budnikov and Cherkasova [659] showed that helenite, which was previously regarded as a hydraulically inactive part of cements, undergoes hydration in the presence of $Ca(OH)_2$ to form calcium hydrosilicates and hydroaluminates, and in the presence of SO_4 ions in the solution to form calcium hydrosulfoaluminate as well. In another recent study [660], it was established that the effectiveness with which γ-$2CaO \cdot SiO_2$ is hydrated diminishes considerably in the presence of the β-modification of dicalcium silicate, and in the presence of sesquioxides in the initial mixture. In the absence of these compounds, the γ-modification of $2CaO \cdot SiO_2$ undergoes hydration in much the same way as the β-modification of this silicate. The activity of cement-clinker minerals in reactions with water, particularly for such important minerals as alite and belite, depends on the defect nature of their structure. Yung, Butt and Timashev [661-663] showed that from this standpoint, prolonged sintering at moderate temperature is less expedient than raising the temperature of the process: long holding eliminates the defects that the crystals acquired in the process of rapid growth and homogenizes their structure; this naturally results in a drop in their activity.

In the synthesis of alite $3CaO \cdot SiO_2$, the third calcium oxide molecule is less strongly bonded than the first two. Yung and Timashev [661] demonstrated this by the tagged-atom method. Synthesizing alite by two possible variants of the process

1) $2CaO \cdot SiO_2 + CaO^* \rightarrow 2CaO \cdot SiO_2 \cdot CaO^*$,
2) $2CaO^* \cdot SiO_2 + CaO \rightarrow 2CaO^* \cdot SiO_2 \cdot CaO$
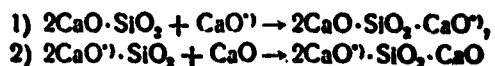
(where the asterisk indicates radioactivity), and then decomposing

- 503 -

the minerals obtained at temperatures of 1175 and 2000°, these authors established that in the decomposition of $3CaO \cdot SiO_2$, the lime that has been added to the dicalcium silicate as the third molecule is liberated first.

In general, the proportions among the minerals of cement clinker and their crystalline structures are held within the necessary limits by strict control of the charge composition and firing conditions.

Research that has recently been done in this direction has led to new inferences concerning the conditions of cement-clinker mineral formation and to the development of techniques for producing bonding materials that possess valuable technical properties. Thus, Yung, Butt and Timashev [661, 664] suggest on the basis of study of calcium aluminoferrites that the alumina is not simply distributed uniformly in the lattice of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in their synthesis, forming a more or less homogeneous solid solution of a given concentration, but retains its order and its structure in this new complex lattice. According to communications from the authors of [661, 664], given an alumina modulus p = 1.79, the formation reaction of celites may be conceived of as taking place between appropriate quantities of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The formation of celites, which differ in composition from the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ taken as a basis for calculations, during firing of the clinker requires that the procedure for computing the recipes be refined. Since mixtures with a modulus p < 1.79 contain cements that are more highly saturated with lime (the lime theoretically belonging to the tricalcium silicate), the actual saturation factor of the mixture is lower than its theoretical value, with the result that the actual content of alite in the clinker is smaller. On this basis, the theoretical value of the saturation coefficient for certain mixtures might be increased above unity to advantage.

Budnikov and Sologlubova [665] established that when a mixture of kaolin with chalk (or limestone) is fired at 1200° in the presence of 10% of gypsum, the result may be the so-called white cement (with a whiteness factor of 85–87), which consists basically of $CaO \cdot Al_2O_3$ and $2CaO \cdot SiO_2$. When it is ground together with 5% of anhydrite, we obtain a mineral that possesses an ultimate compressive strength of 575 kg/cm^2 6 months after setting.

The quick-setting grade 800 high-strength cement developed by Strelkov [666] contains (in %): $3CaO \cdot SiO_2$ — 50 $\pm$ 2, $3CaO \cdot Al_2O_3$ — 8 $\pm$ 0.5, $4CaO \cdot Al_2O_3 \cdot FeO_3$ — 10 $\pm$ 0.5, less than 0.15 of alkalis, 2.75 $\pm$ $\pm$ 0.25 of SO_3, and traces of free CaO. With a specific surface of 6000 cm^2/g, a cement of such a composition that also contains 27.8% of di-calcium silicate shows compressive strengths of 400, 587, 705 and 821 kg/cm^2, respectively, in a hard-consistency mortar after 1, 3, 7 and 28 days.

Tests of specimens of grade 800 cement that had been stored under standard conditions showed that its strength in mortars of both hard and plastic consistencies increases in time up to 1 year. Thus, the strength of a cement having an activity of 855 kg/cm^2 had reached the very high value of 970 kg/cm^2 after 1 year [666].

An important problem is that of the physical state of the reacting substances in the formation of cement clinker. It is now generally known that at the maximum firing temperature, no less than 25-35% of the initial quantity of the reaction mixture is in the liquid state; part of this liquid remains uncrystallized even in the cooled clinker. It has been established [667] that even at a temperature as low as 1338°, all of the ferric oxide, about 70% of the aluminum oxide, 20% of the calcium oxide and 5% of the silicon dioxide present in the mixture of these oxides corresponding to the composition of Portland

cement is in the liquid phase. The most important reactions forming the minerals of cement clinker under practical conditions take place by interreaction between the liquid and crystalline phases, and some of these minerals (for example, ferrites, tricalcium aluminate, tricalcium silicate) form directly in the melt, from which they subsequently crystallize [316, 656, 661-663, 667].

Bog [667], the well-known specialist in the field of cement chemistry and technology, regards it as generally acknowledged at the present time that processes of fusion, solution and precipitation are more important for the production of cement clinker than processes related to the reaction capability of the solid phases.

In view of this, and since "the principles of interaction between a solid and a liquid due to diffusion are similar to those pertaining to interactions between two solids with surfaces in intimate contact," he assumes that in considering the reactions of cement-clinker mineral formation, we may specifically disregard the physical state of the latter body; it is sufficient that "one reagent is always assumed to be in the solid state."

Having stressed the importance of the position accorded by Bog to the liquid phase in the above reactions, we shall not dwell in this case on the importance of analysis and deliberate regulation of the part that it plays, since these problems have been analyzed in detail above as they affect all reactions in crystalline mixtures in general.

The cement clinker obtained in practice is not in an equilibrium state. Three causes of this nonequilibrium and three forms that it takes can be noted:

1) the incompleteness of the reactions between the residual calcium oxide and the previously formed calcium orthosilicate, as a re-

sult of the inadequate speed of these reactions;

2) deviations from equilibrium crystallization of the liquid phase due to the usually very short time allowed for cooling the clinker as compared with the time that would be necessary for the equilibrium-crystallization process;

3) phase-composition nonuniformity, which gives rise to various types of diffusion resistances to the attainment of heterogeneous equilibrium (isolation of individual grains, and so forth).

The above circumstances sometimes result in essential departure of the actual composition and properties of the clinker from those expected on the basis of stoichiometric calculations and laboratory tests.

The formation of the following solid solutions exerts a considerable influence on the processes of cement-clinker formation and on its properties: tricalcium aluminate-tricalcium silicate [668], dicalcium ferrite-dicalcium aluminate [669 - 671], pentacalcium trialuminate-dicalcium ferrite-calcium oxide [672, 673], tetracalcium aluminoferrite-dicalcium ferrite [653], alkali-alumina-dicalcium silicate [602] and others.

The great importance of mass transfer in the formation reactions of cement clinker and the limiting of their rate by diffusion phenomena make it extremely important to regulate them with the so-called mineralizers (see §2 of Chapter 7).

In practice, calcium fluoride in the form of natural fluorspar is most widely employed as an accelerator for these reactions. In the USSR, the first experiments in its use were conducted as long ago as 1933 by Makashev and Royak [674, 675]. Now, as a result of the investigations of Royak, Makashev [676], Toropov et al. [316, 409, 677], Yung and Azelitskaya [678] and many other authors (see, for example,

[679-681]), it has been established that the rate of silicate formation and the rate of volatilization of the alkaline oxides are raised considerably in the presence of 0.7-1.5% of fluorides, referred to the weight of the reaction mixture, and that it is not advisable to increase the fluoride content greatly; the effectivenesses of various accelerators in promoting the roasting process at various temperatures have been described, the importance of the structure and viscosity of the liquid phase (that appears in the presence of a fluxing mineralizer) in determining the process rate has been pointed out, and so forth. However, the question of mineralizers in the chemistry and technology of cements is nevertheless the least studied aspect; this is due chiefly to the inadequate development of the general theory of accelerators for reactions in solids.

Let us note, finally, the essential influence of fuel composition and gaseous phase (roasting atmosphere) on the direction and rate of the reactions described and on the composition and properties of the clinker produced. Naturally, the ash content and ash composition of the fuel (its contents of R_2O, R_2O_3, RO) cannot but be reflected to some degree in the conditions and results of the roasting process. As concerns the composition of the gaseous phase, the positive influence of water vapor in it, together with the smallest possible quantity of oxygen, is a known fact. Regulation of the latter's content within strict limits is, in certain cases, the most important condition for successful conduct of the process, as, for example, was established by Royak [320] in his time in the production of cement from gypsum.

The influence of all these factors on the process as a whole cannot, naturally, be fully understood and deliberately exploited for practical purposes without profound study of the reactions described

above and the conditions for conducting them in practice.

Manu- script Page No.	[Footnotes]
493	G.A. Smolenskiy, Izv. AN SSSR, Ser. Fiz [Bulletin of the Acad. Sci. USSR, Physics Series], 16, 728 (1952); Usp. fiz. nauk [Progress in the Physical Sciences], 62, No. 1, 41 (1957); A.G. Gurevich and V.A. Isupov, article in the collection Poluprovodniki v nauke i tekhnike [Semiconductors in Science and Technology] (Edited by A.F. Ioffe), Izd. AN SSSR [Acad. Sci. USSR Press], 1958.
497	We also obtain the properties of the ceramic pigments described by S.G. Tumanov (S.G. Tumanov, articles in the collection Fizikokhimicheskiye osnovy keramiki [Physicochemical Bases of Ceramics], Promstroyizdat, Moscow, 1956.

CONCLUSION

As a result of numerous research studies, science now has at its disposal an extremely rich body of data on reactions in solids (the information presented in this book, it goes without saying, gives only a partial representation of it). On the basis of theoretical premises and experimental data of the chemistry of crystalline solids, the possibility of producing an enormous number of diverse technically important substances by reactions in crystalline mixtures has been opened, optimum conditions have been found for the practical conduct of many such reactions, and technological processes have been developed and realized for the production of various products in various branches of engineering.

However, life and practical work continuously place new and serious problems before the investigators in this field of knowledge.

It is known that the grandiose plans for the development of our national economy require the creation of new high-quality refractory, structural and other materials.

The seven-year plan now being implemented provides, among other things, for considerable development of the structural-materials industry, and primarily an expansion of the production of quick-setting cement; essential development and intensification of the metallurgical and chemical industries (and, in particular, of the coke-chemical industry) involving increased output and quality improvements for high-refractory, acid-resistant and other similar materials; further development of thermal- and electric-power engineering and of the elec-

trical-engineering and radio-engineering industries, semiconductor technique, automation of production processes, which require considerable improvement and development of the production, respectively, of heat- and electrical-insulation materials, radioceramic semiconductor and other materials obtained by reactions in crystalline solids.

Many of the processes being used in industry and based on reactions in solid mixtures require radical reworking to increase their efficiency; this can be done only as a result of profound understanding of their nature and most important qualitative laws. These processes include the production of cement clinker and a number of refractory materials, roasting nonferrous-metal ores, sintering the charges for alumina production, and many others.

Certain new fields of engineering are submitting extremely rigid requirements for refractory materials: they must possess negligible, near-zero porosity and stability at very high temperatures that diverge widely even from the temperatures normally employed in metallurgical processes. This makes it necessary to create new materials and develop new recipes and production processes.

Finally, the development of certain new high-efficiency industrial processes requires basically new solutions to problems related to the conduct of reactions between solids (suspension-layer roasting, and others).

All this necessitates further profound study of reactions in crystalline mixtures.

It will be appropriate to dwell on certain basic problems encountered in this study.

Efforts to produce industrial products with rigorously prespecified chemical, mechanical, thermal, optical and sometimes electrical, magnetic and other properties make it necessary in the case of crys-

talline-mixture reactions to conduct basic research into the dependence of these properties on the chemical, granulometric and phase compositions of the initial mixtures, on their crystalline structure, on the structure of the starting materials and intermediate compounds, on the temperature conditions of the reaction, and so forth.

For this reason, numerous research studies are justifiably being devoted at the present time to the problem of the product properties as functions of the factors determining them, understanding the action of these factors, and establishing control over them. The relationship between the properties of crystalline solids and the nature and concentration of the defects present in them occupies a central position in this problem. The possibility and methods of sufficiently rigorous, deliberate control of the properties of a solid by varying the nature and degree of disturbance of its lattice will undoubtedly become the object of systematic study at least during the next few decades. The theoretical and practical importance of this problem, to which inadequate attention is now being devoted, will hardly require any further explanation.

Investigations of the above trend include, among others, study of the processes in which quick-setting cements and various types of refractory materials are produced.

The term "quick-setting" is, as we know, applied to a cement that is capable of developing no less than 50% of its 28-day strength within one day and no less than 80% of this strength in 3 days. The value of a cement possessing such properties is obvious. At the present time, the production of prefabricated reinforced-concrete structures and structural elements is undergoing intensified development in the Soviet Union; this requires large quantities of cement with a high early strength.

It has been established by research that the basic condition for producing such a cement is careful regulation of the mineralogical and granulometric composition of the clinker. The influence exerted by certain additives on the setting rate of cement has been established experimentally. However, there is still much important work to be done in this direction.

Forced operation of metallurgical and, in particular, open-hearth furnaces requires that the stability of all basic structural elements be improved. Investigation related to this problem has led to important helpful results. Thus, the introduction of thermostable chromomagnesite brick for lining the hearths of open-hearth furnaces has made it possible to increase their productivity and service life considerably. However, the extremely rigid specifications set forth for the furnace components, which differ for different elements, are obliging investigators to work on improved quality in present refractory materials and to create new ones. In this respect, an important role is apparently in store for the forsterite refractories, which are highly stable under the operating conditions of many units of the open-hearth furnace and whose production requires raw-material resources of which our country has an inexhaustible supply. Consequently, persistent study of the processes in which these refractories are made and ways to improve their quality is fully justified. Studies have been initiated in this field to assist in solving the important problem of raising the stability of all open-hearth furnace elements for intensified operation.

One of the most important problems in solid-state chemistry is study of the processes in which new high-refractory materials may be produced. It is known that such oxides as MgO, BeO, Al_2O_3, ZrO_2, ThO_2, UO_2 and certain others serve as bases for the successful formation of

materials that undergo virtually no changes at very high temperatures. During the last few years, striking progress has been made in this field. Practically important investigations have been conducted into the processes in which certain crystalline solids possessing the above properties are produced.

However, the theory of these processes, methods for controlling them and ways to regulate the properties of their products have been the subject of quite inadequate study. Only spotty information is presently available concerning certain reactions in systems containing zirconium dioxide, thorium dioxide and uranium dioxide. Technique is inadequately developed and theory neglected in the case of such a promising method for producing high-refractory materials possessing great density as hot pressforming. It is therefore necessary to prosecute even further the development of theoretical and experimental work in this field, including studies related to the use of the hot-pressforming method with crystalline solids.

The problems of complex processing of raw materials and the universal use of readily accessible and, if possible, local forms of raw material require profound study of ways to produce refractory, adhesive and other materials from substances that are unused or little used at the present time for these technological purposes.

Much work is, of course, being done in this direction, but the scale on which it is being done is still lagging behind the requirements of the economy. The problem of full and efficient utilization of local limestones and clays, natural gypsum, shales and also such industrial wastes as metallurgical slags, phosphogypsum, roasted pyrites, and the like requires a considerable expansion of research in this field.

The most important problems of the study of intersolid reactions

includes investigation of the rate of these reactions as a function of the factors determining it, finding methods for deliberate and sufficiently precise and dependable control of it, and ways for radical intensification of reactions between solids.

The means necessary for control of the rate of such reactions are, as we know, control of the grain size of the initial reagents, of the process temperature, and of the content of the various additives that accelerate or stabilize the process in the reaction mixture. Proper utilization of each of these tools and justified selection of various combinations of them will naturally be possible only from profound understanding of the basic nature of their action. However, the mechanism by which many accelerators affect these reactions — particularly in the case of certain accelerators for the cement-clinker process — has not been definitely ascertained to the present day. Thus far, no general rigorous criterion and no consistent method for evaluating and comparing the performances of different accelerators have been established. Also inadequately studied and unclear are the mechanisms of many crystalline-mixture reactions.

Deliberate control of the rate of a process naturally pre-supposes knowledge of the laws governing its variation under various conditions. At the same time, the laws governing the variation of reaction rates in crystalline mixtures remain neglected by research for certain conditions (particularly in the transitional region, when both micro- and macroprocesses exert an essential influence on the process rate).

The importance of studying the mechanism and kinetics of reactions in mixtures of solids under various conditions becomes particularly clear in the light of these statements. Systematic studies in this direction are of great fundamental theoretical importance and

will open broad vistas for the practical utilization of reactions between solids.

Here, it is obvious that understanding of the essence and qualitative laws of reactions in crystalline-reagent mixtures will require study of the mechanism and qualitative laws of all of the "elementary" processes described above and composing these reactions, and the relationships between them under practical conditions.

During the last few years, many studies have been carried out in the field of polymorphic transformations, the formation and decay of solid solutions, diffusion in solids, sintering and recrystallization. However, the theory of these processes has as yet undergone far from adequate development, and the experimental data on them are full of basic contradictions. This applies in particular to such important processes as sintering and polymorphic transformations (for example, the transformations of silica), which also have independent technical significance.

At the present time, we may encounter in the literature the most widely divergent judgments as to the nature and qualitative laws of the processes of "dry" and wet sintering and their influence on other processes that take place when crystalline mixtures are heated. There are at least ten theories of the sintering process. The validity of none of them has as yet been definitely proven.

The part taken by lattice distortions (including the relationship between any distortion characteristic and the self-diffusion coefficient) remains inadequately studied, as do the parts taken by impurities and surface diffusion in the sintering process, its characteristics in the presence of pores of various sizes in the body, and the pattern in which various factors, such as temperature and pressure, influence it simultaneously.

- 516 -

The problem of the influence of composition and properties of the liquid phase on the mechanism and kinetics of liquid sintering merits further theoretical and experimental investigation.

Deliberate and precise control of conversion processes in crystalline mixtures requires profound understanding and study of the mechanism and laws of all stages composing these processes. This requires systematic collaboration among chemists, physicists and engineers.

At the present time, this work has come up against serious difficulties of experimental as well as theoretical nature. In the majority of cases, the researcher has no way of determining small contents of impurities adsorbed on the surfaces and in the bulk of solids, and no way to free them completely of these impurities: known methods of chemical analysis and purification of materials are inadequate for this purpose.

Existing experimental research methods also limit the possibility of detecting small structural changes and small quantities of new (particularly liquid) phases in the objects of study. Finally, it is very often impossible to make continuous observation of changes in solids during their physicochemical transformation at high temperatures, either directly or even indirectly. In these cases, inferences as to the course taken by the process in time are drawn from examination of specimens that have been under the conditions of the reaction for various intervals of time and then cooled.

The importance of all these circumstances and the possibility of distorting the true picture of the process are unquestionable. We recall that the presence, for example, of very small amounts of impurities over a liquid phase in the system is capable of working profound changes in the mechanism and kinetics of a solid-mixture reac-

tion.

Inadequate purity of the starting reagents and disregarding (in inferences and conclusions) the impurities present in them result, as we know, in serious errors in judging questions of reaction mechanism in solids.

Consequently, the development and use of sufficiently rigorous and dependable methods for purifying and investigating the solid, methods that enable us to control quantitatively relatively small (but essentially important) changes in its structure and phase and chemical composition are absolutely necessary for further research into crystalline-mixture reactions.

In summarizing all the above, we must conclude that there are still many unsolved problems confronting us: the contemporary state of study of solid-state reactions requires urgent development of theoretical and experimental studies in this field. These studies will undoubtedly contribute to successful solution of many problems associated with the most important tasks of progress in various branches of engineering.

REFERENCES

1. P.P. Budnikov and A.S. Berezhnoy, Reaktsii v tverdykh fazakh [Reactions in Solid Phases], Promstroyizdat [State Publishing House of Literature on Building Materials], 1949.

2. F.M. Flavitskiy, Retsept [Compounding], No. 6, 82 (1902).

3. Ye.S. Fedorov, Simmetriya i struktura kristallov [Symmetry and Structure of Crystals], Izd. AN SSSR [Publishing House of the Acad. Sci. USSR], Moscow, 1949.

4. D.I. Blokhintsev, Osnovy kvantovoy mekhaniki [Fundamentals of Quantum Mechanics], Izd. tekhn.-teor. lit. [Publishing House for Technical and Theoretical Literature], Moscow-Leningrad, 1949.

5. L.D. Landau and Ye.M. Lifshits, Statisticheskaya fizika [Statistical Physics], GTTI [State Technical Theoretical Editions], Moscow-Leningrad, 1951.

6. R. Payerls, Kvantovaya teoriya tverdykh tel [Quantum Theory of Solids], IIL [Foreign Literature Publishing House], Moscow, 1956.

7. G. Eyring, Dzh. Uolter and Dzh. Kimball, Kvantovaya khimiya [Quantum Chemistry], IIL, Moscow, 1948.

8. G.B. Bokiy, Vvedeniye v khristallokhimiyu [Introduction to Crystal Chemistry], Izd. Mosk. universiteta [Publishing House of Moscow University], Moscow, 1954.

9. V.M. Goldschmidt, Ber. d. Chem. Ges. [Reports of the Chemical Society], 60, 1263 (1927).

10. L. Pauling, Priroda khimicheskoy svyazi [The Nature of the Chemical Bond], Goskhimizdat [State Scientific and Technical Publishing House of Chemical Literature], Moscow-Leningrad, 1947.

11. N.V. Belov, Struktura ionnykh kristallov i metalicheskikh faz [Structure of Ionic Crystals and Metallic Phases], Izd. AN SSSR, Moscow, 1947.

12. G.M. Popov and N.I. Shafranovskiy, Kristallografiya [Crystallo-graphy], Gosgeoltekhizdat [State Scientific and Technical Publishing House of Literature on Geology and the Conservation of Mineral Resources], Moscow, 1955.

13. G. Mie, Ann. d. Phys. [Annals of Physics], 11, 657 (1903).

14. O. Rays, Elektronnoye stroyeniye i khimicheskaya svyaz' [Electronic Structure and the Chemical Bond], IIL, Moscow, 1949.

15. B.F. Ormont, Struktury neorganicheskikh veshchestv [The Structure of Inorganic Substances], CTTI, Moscow-Leningrad, 1950.

16. M. Born and Khuan Kun', Dinamicheskaya teoriya kristallicheskikh reshetok [Dynamic Theory of Crystal Lattices], IIL, Moscow, 1958.

17. B.N. Finkel'shteyn, Fizicheskoye metallovedeniye [Physical Metallurgy], Collection, Metallurgizdat [State Scientific and Technical Publishing House for Literature on Ferrous and Nonferrous Metallurgy], Moscow, 1955.

18. A.A. Litvakovskiy, St. v sbornike nauchnykh rabot po khimii i tekhnologii silikatov, posvyashchennom 70-letiyu P.P. Budnikova [Article in a Collection of Scientific Works on Chemistry and Technology Devoted to the Seventieth Birthday of P.P. Budnikov], 283, Promstroyizdat, Moscow, 1956.

19. A.F. Kapustinski, Z. Krist. [Journal of Crystallography], 86, 350 (1933); ZhFKh [Journal of Physical Chemistry], 1, 59 (1934).

20. A.F. Kapustinskiy, Acta Physico-chim., USSR, 38, 370 (1943), ZhOKh [Journal of General Chemistry], 13, 496 (1943); Quarterly Reviews, 10, 283 (1956).

21. A.F. Kapustinskiy and K.B. Yatsimirskiy, ZhOKh [Journal of General Chemistry], 26, 941 (1956).

22. B.V. Nekrasov, Kurs obshchey khimii [Course in General Chemistry], Goskhimizdat, Moscow-Leningrad, 1953.

23. W.E. Garner (Ed.), Chemistry of the Solid State, London, 1955.

24. R. Shuttleworth, Proc. Phys. Soc. Lond., A 62, 167 (1949).

25. P.A. Rebinder, Tverdost', Tekhn. Ents. [Hardness, Technological Encyclopedia], 22, 703, 1933.

26. P.A. Rebinder, N.A. Kalinovskaya, M. Linets et al., Issledovaniye v oblasti poverkhnostnykh yavleniy [Research in the Region of Surface Phenomena], ONTI [United Scientific and Technical Publishing Houses], 1936.

27. P.A. Rebinder, Vestnik AN SSSR [Bulletin of the Acad. Sci. USSR], 10, No. 85, 9 (1940).

28. V.D. Kuznetsov, Fizika tverdogo tela [Physics of Solids], 1, Tomsk, 1937.

29. V.D. Kuznetsov, Poverkhnostnaya energiya tverdykh tel [Surface Energy of Solids], GTTI, Moscow, 1954.

30. M. Renninger, Z. f. Kristallographie [Journal for Crystallography], 89, 344 (1934).

31. C.A. Cinnamon and A.B. Martin, J. Appl. Phys., 11, 487 (1940).

32. O.F. Tuttle and W.S. Twenhofel, Am. Mineral, 31, 569 (1946).

33. A. Riz, Khimiya kristallov s defektami [Chemistry of Crystals with Defects], IIL, Moscow, 1956.

34. F. Seitz, Imperfections in Nearly Perfect Crystals, 1953.

35. Ye.S. Federov, Priroda [Nature], 1471 (1915).

36. A. Smecal, Handbuch der Physik [Handbook of Physics], 24, 795 (1933); Int. Conf. Phys., 2, 93 (1934).

37. A.F. Ioffe, Int. Conf. Phys., 2, 77 (1934).

38. F. Zwicky, Proc. Nat. Acad. Sci. U.S., 15, 253, 816 (1929); Phys. Rev., 38, 1772 (1931); 40, 62 (1932); Rev. Mod. Phys., 6, 193 (1934).

39. D. Balarew, Kolloid-Beihefte [Colloid Reference Numbers], 32, 205

(1931); 37, 180 (1933); 50, 1 (1939).

40. J.H. Boer, Electron Emission and Adsorption Phenomena. Cambr., 1935.

41. H. Mott and R. Gerin, Elektronnyye protsessy v ionnykh kristallakh [Electronic Processes in Ionic Crystals], IIL, 1950.

42. Ya.I. Frenkel', Kineticheskaya teoriya zhidkostey [Kinetic Theory of Liquids], Izd. AN SSSR, 1945.

43. Ya.I. Frenkel', Vvedeniye v teoriyu metallov [Introduction to Theory of Metals], Izd. tekhn.-teor. lit., 1950.

44. Ya.I. Frenkel', Teplovoye dvizheniye v tverdykh i zhidkikh telakh i teoriya plavleniya [Thermal Movement in Solids and Liquids and Theory of Fusion], VSNITO [All-Union Council of Scientific, Engineering and Technical Societies], Moscow, 1936.

45. Ya.I. Frenkel', Teoriya tverdykh i zhidkikh tel [Theory of Liquids and Solids], GTTI, Leningrad-Moscow, 1934.

46. G. Bakli, Rost kristallov [The Growth of Crystals], IIL, 1954.

47. M.Yu. Bal'shin, Vestnik Metallopromyshlennosti [Herald of the Metals Industry], 17, 87 (1936); ZhTF [Journal of Technical Physics], 22, No. 4, 686 (1952); Poroshkovoye metallovedeniye [Powder Metallurgy], Metallurgizdat, Moscow, 1948.

48. E. Orowan, Z. Phys. [Journal of Physics], 79, 573 (1932); 89, 774 (1934).

49. A.S. Berezhnoy, Ogneupory [Refractory Materials], No. 7, 307 (1954).

50. I.S. Kaynarskiy and S.L. Lesnichenko, Ogneupory, No. 4, 162, 1948.

51. J. Grzymek, Przemysl Chemiczny [Chemical Industry], 21, 279 (1937); Trudy soveshchaniya po khimii tsementa [Trans. of Conference on the Chemistry of Cement], 27, Promstroyizdat, Moscow, 1956.

52. J.A. Hedvall, Arkiv Kemi [Archives of Chemistry], 6, No. 19,

241 (1953).

53. S.Ye. Andreyev, V.V. Tovarov and V.A. Perov, Zakonomernosti iz-
mel'cheniya i ischisleniye kharakteristik granulometricheskogo
sostava [Laws of Pulverization and Calculation of Characteristics
of Granulometric Composition], Gosmetallurgizdat, 1959.

54. G.I. Preygerzon, Obogashcheniye ugiya [Coal Dressing], Ugletekh-
izdat [State Scientific and Technical Publishing House of Liter-
ature on the Coal Industry], Moscow-Leningrad, 1948.

55. Spravochnik po obogashcheniyu poleznykh iskopayemykh [Handbook
on Dressing of Useful Minerals], Vol. 4, 436, Metallurgizdat,
Moscow, 1950.

56. A. Uorsing and Dzh. Geffner, Metody obrabotki eksperimental'nykh
dannykh [Methods of Processing Experimental Data], IIL, Moscow,
1949.

57. A.M. Ginstling, ZhPKh [Journal of Applied Chemistry], 24, 566
(1951).

58. R. Holm, Wiss. Veroef. Siemens. Konz. [Sci. Pub. Siemens Concerns],
7, No. 2, 217 (1922); 9, No. 2, 300, 312, 323 (1930); 10, No. 4,
1, 20 (1931); 15, No. 1, 122 (1936).

59. F.P. Bowden and D. Tabor, Proc. Roy. Soc., 169, 391 (1939).

60. N.K. Adam, Fizika i khimiya poverkhnostey [Physics and Chemistry
of Surfaces], Izd. tekhn.-teor. lit., Moscow-Leningrad, 1947.

61. Dzh. Mak-Ben, Sorbtsiya gazov i parov tverdymi telami [Sorption
of Gases and Vapors by Solids], Goskhimtekhizdat, 1934.

62. R. Barta, O reakcich v tuhem stavu [Solid-State Reactions], Praha
[Prague], 1954.

63. V.D. Kuznetsov, Kristally i kristallizatsiya [Crystals and Crys-
tallization], GTTI, Moscow, 1954.

64. W. Trzebiatowsky, Z. phys. Chem. [Journal of Physical Chemistry],

B-24, 75, 87 (1934); A 169, 91 (1934).

65. N.Ye. Pestov, Fiziko-khimicheskiye svoystva zernistykh i porosh-
kovykh khimicheskikh produktov [Physicochemical Properties of
Granular and Powdered Chemical Products], Izd. AN SSSR, Moscow-
Leningrad, 1947.

66. N.S. Kurnakov, Rastvory i splavy (stat'ya v "Osnovakh khimii"
D.I. Mendeleyeva [Solutions and Alloys (paper in book entitled
"Principles of Chemistry" by D.I. Mendeleyev)], 9th Edition, GIZ
[State Publishing House], 1928.

67. Ye.S. Makarov, Stroyeniye tverdykh faz s peremennym chislom
atomov v elementarnoy yacheyke [Structure of Solid Phases With
Variable Number of Atoms in Elementary Cell], Izd AN SSSR, Moscow-
Leningrad, 1947; Doctorate Dissertation, IONKh AN SSSR [Institute
of General and Inorganic Chemistry (im. N.S. Kurnakov) Acad. Sci.
USSR], Moscow, 1953.

68. Ye.S. Makarov, Izvestiya sektora fiz.-khim. analiza [Bulletin of
the Department of Physical and Chemical Analysis], IONKh AN
SSSR, 16, 149 (1943).

69. Ya.S. Umanskiy and S.S. Khidekel', ZhFKh [Journal of Physical
Chemistry], 15, No. 9, 983, 997 (1941).

70. Ya.S. Umanskiy, Karbidy tverdykh splavov [Carbides of Solid
Alloys], Metallurgizdat, 1947.

71. A.Kh. Breger, Acta Physico-chim., USSR, 13, 600 (1940).

72. V.D. Kuznetsov, Izvestiya sektora fiz.-khim. analiza, IONKh AN
SSSR, 16, No. 4, 68, 151 (1948).

73. L. Vegard, Z. Phys., 5, 393 (1921).

74. B.Ya. Pines, ZhETF [Journal of Experimental and Theoretical
Physics], 11, 147 (1941).

75. J. Groh, G. Hevesy, Ann. d. Phys., 63, 85 (1920); 65, 216 (1921).

76. G. Hevesy, Z. Phys., 2, 148 (1920).

77. L.A. Vulis, Stat'ya v Sbornike rabot laboratorii fizicheskoy ognetekhniki [Collection of Works of the Laboratory of Physical Pyrotechnics], TsKTI [Central Scientific Research Institute for Boilers and Turbines], Energoizdat, Moscow, 1948; ZhTF, 10, 23, 1959 (1940); 11, 509 (1941).

78. K. Fischbeck, Z. Electrochem. [Journal of Electrochemistry], 39, 316 (1933); 40, 517 (1934).

79. D.A. Frank-Kamenetskiy, Diffuziya i teploperedachi v khimicheskoy kinetike [Diffusion Heat Transfer in Chemical Kinetics], Izd. AN SSSR, Moscow-Leningrad, 1947; ZhFKh, 13, 756 (1939); Uspekhi khimii [Progress in Chemistry], 7, 1277 (1938); ZhTF, 10, 1207 (1940).

80. B. Sen, Compt. rend. Acad. Sci., 199, 1189 (1934).

81. H. Braune, Z. phys. Chem., 110, 147 (1924).

82. A.D. Smigeskas and E.O. Kirkendall, Metals Technology, 13 (1946), Techn. Publ. No. 2071; Trans. Am. Inst. Min. Met. Eng., 171, 130 (1947).

83. B.Ya. Pines, Usp. fiz. nauk [Progress in the Physical Sciences], 52, 501 (1954).

84. B.Ya. Pines and Ya.S. Geguzin, ZhTF, 23, No. 9, 1959 (1953).

85. A.F. Ioffe, Ann. d. Phys., 72, 461 (1923).

86. Ya.I. Frenkel', Ztschr. Phys. [Journal of Physics], 35, 652 (1926).

87. F. Zeytts, Sovremennaya teoriya tverdogo tela [Modern Theory of Solids], GTTI, Moscow-Leningrad, 1949.

88. R. Berrer, Diffuziya v tverdykh telakh [Diffusion in Solids], IIL, Moscow, 1948.

89. W. Jost, Diffusion in Solids, Liquids and Gases, New York, 1952.

90. H.B. Huntington ano F. Seitz, Phys. Rev., 61, 315, 325 (1942).

91. M.A. Bol'shanina and V.Ye. Panin, Sbornik. Issledovaniya po fizike tverdogo tela [Collection. Research on the Physics of Solids], 193, Izd. AN SSSR, Moscow, 1957.

92. N.F. Mott, Proc. Phys. Soc., 60, 391 (1948); 64, 729 (1950).

93. L.M. Clarebrough, M.E. Hargreaves and G.W. West, Proc. Roy. Soc. A215, No. 1123, 22 (1952); A 232, No. 1189, 252 (1955); Phil. Mag., I, No. 6, 528 (1956).

94. L.M. Clarebrough, . M.E. Hargreaves, A.K. Head and G.W. West, Trans. Am. Inst. Min. Met. Eng., 203, (1), 99 (1955).

95. S.L. Sobolev, Uravneniya matematicheskoy fiziki [Equations of Mathematical Physics], Gostekhizdat, Moscow, 1954.

96. I. Crank, The Mathematics of Diffusion, Oxford, 1956.

97. Ya.I. Frenkel', ZhETF, 16, 29, 39 (1946).

98. M. Polyani and E. Wigner, Z. phys. Chem., A 139, 439 (1928).

99. Duschman and I. Langmuir, Phys. Rev., 20, 113 (1922).

100. I.Ya. Dekhtyar, Voprosy fiziki metallov i metallovedeniya [Problems of the Physics of Metals and Metallurgy], No. 2, 144, 158, No. 4, 42. Izd. AN USSR [Publishing House of the Acad. Sci. of the Ukrainian SSR], Kiev, 1950, 1953.

101. V.Z. Bugakov, Diffuziya v metallakh i splavakh [Diffusion in Metals and Alloys], GTTI, Leningrad-Moscow, 1949.

102. M.P. Klibanov, V.V. Pomerantsev and D.A. Frank-Kamenetskiy, ZhTF, 12, 14 (1942).

103. M.A. Krivoglaz and A.A. Smirnov, Teoriya uporyadochivayushchikhsya splavov [Theory of Ordered Alloys], Fizmatgiz, Moscow, 1958; ZhETF, 24, 409, 673 (1953); DAN SSSR, 96, 495 (1954); Voprosy fiziki metallov i metallovedeniya [Problems of the Physics of Metals and Metallurgy], No. 4, 95, Izd. AN USSR, 1953; Usp. fiz. nauk

[Progress in the Physical Sciences], 55, No. 3, 391 (1955).

104. I.Ya. Dekhtyar, Voprosy fiziki metallov i metallovedeniya Sbornik nauchn. rabot lab. metallofiziki AN USSR [Problems of the Physics of Metals and Metallurgy, Collection of Scientific Works of the Laboratory of Metal Physics of the Acad. Sci. of the Ukrainian SSR], No. 3, 122, Izd. AN USSR, Kiev, 1952.

105. M.A. Krivoglaz, DAN USSR, No. 5, 344 (1953).

106. A.A. Smirnov, DAN USSR, No. 5, 351 (1950). Voprosy fiziki metallov i metallovedeniya [Problems of the Physics of Metals and Metallurgy], No. 3, 1943, Izd. AN USSR, 1952; ZhTF, 23, 56 (1953).

107. A.D. Le Claire, Progress in Metal Physics, 4, 265 (1953). Uprugost' i neuprugost' metallov [Elasticity and Inelasticity of Metals], IIL, Moscow, 1954.

108. C. Matano, Jap. J. Phys., 8, 109 (1933); Proc. Phys. Math. Soc. Jap., 15, 405 (1933).

109. L. Boltzmann, Ann. d. Phys., 53, 959 (1894).

110. P.L. Gruzin, Yu.V. Kornev and G.V. Kudryumov, DAN SSSR, 80, No. 1, 49 (1951); Problemy metallovedeniya i fiziki metallov [Problems of Metallurgy and the Physics of Metals], Collection 3, 201, 226, Goametallurgizdat, 1952.

111. S.D. Gertskriken and P.Ya. Dekhtyar, Voprosy fiziki metallov i metallovedeniya [Problems of the Physics of Metals and Metallurgy], No. 2, 108, Izd. AN USSR, Kiev (1950).

112. F. Seitz, Phys. Rev., 74, 1513 (1948).

113. M. Volmer and J. Estermann, Z. Phys., 7, 13 (1921).

114. M. Volmer and G. Adhikari, Z. Phys., 35, 170 (1925), Z. Phys. Chem., 119, 46 (1926).

115. M. Volmer, Trans. Farad. Soc. 28, 359 (1932).

116. I. Langmuir, J. Franklin Inst. 217, 543 (1934).

117. R. Bosworth, Proc. Roy. Soc., 150A, 58 (1935), 154A, 112 (1936).

118. I. Weier, Z. anorg. allg. Chem., 209, 409, 1932.

119. N.A. Toropov, G.P. Dmitriyev and L.D. Merkov, Trudy Petrografi-
cheskogo instituta AN SSSR [Trans. of the Petrographic Institute
of the Acad. Sci. USSR], No. 10, 169 (1937).

120. A.M. Ginstling, Stat'ya v sbornike fiziko-khimicheskiye osnovy
keramiki [Articles in Collection entitled Physicochemical Bases
of Ceramics], Promstroyizdat, 1956.

121. G.A. Meyerson, I.M. Fedorchenko and V.A. Ivensen, Stat'i v sb.
voprosy poroshkovoy metallurgii (Trudy 2-y kiyevsk. n.-t. sessii
po vopr. poroshk. metallurgii) [Articles in Collection Entitled
Problems of Powder Metallurgy (Trans. of the Second Kiev Scien-
tific-Technical Session on Problems of Powder Metallurgy), 16,
53, 130, Izd. AN USSR, Kiev, 1955.

122. V.A. Ivensen, ZhTF, 17, 1301 (1947); 18, 1290 (1948); 20, 1483,
1490 (1950); 22, 677 (1952); 23, 183 (1953).

123. N.T. Gudtsov, M.Yu. Bal'shin, V.S. Rakovskiy (Editorial Board),
Poroshkovaya metallurgiya (trudy nauchno-tekhnicheskoy sessii)
[Powder Metallurgy (Trans. of Scientific-Technical Session)],
Gosmetallurgizdat, Moscow, 1954.

124. D.R. Wilder and E.G. Fitzimmons, J. Am. Ceram. Soc., 38, 66 (1955).

125. B.Ya. Pines, ZhTF, 16, 737 (1946).

126. Ya.Ye. Geguzin, L.O. Morkon and B.Ya. Pines, DAN SSSR, 87, No. 4,
572 (1952).

127. F.N. Rhines, C.E. Birchenall and L.A. Hughes, J. Metals, 188,
378, 1950.

128. I.Ye. Dudavskiy and G.V. Kukolev, Trudy Ukr. In-ta ogneuporov
[Trans. of the Ukrainian Institute of Refractory Materials],
No. 46, 25 (1941).

129. G.A. Gich, Stat'ya v sb. Uspekhi fiziki metallov, perevod s

nemetskogo pod red. Ya.S. Umanskogo and B.M. Finkel'shteyna iz "Progress in Metal Physics" [Articles in Collection Entitled Progress in Metal Physics, Translation from the German Edited by Ya.S. Umanskiy and B.N. Finkel'shteyn], GNTI Metallurgii, Moscow, 1956.

130. H.H. Hausner, N.P. Pinto, A.S.M. Preprint, 38, 1950.

131. A.I. Leonov, Izvestiya AN SSSR OKhN [Bull. Acad. Sci. USSR, Department of Chemical Sciences], No. 5, 805 (1955).

132. P.W. Clark, J. White and J.H. Cannon, Trans. Brit. Ceram. Soc., 49, 305 (1950); 52, 1 (1953).

133. G. Grube and H. Schlecht, Z. Electrochem., 44, 367 (1938).

134. A.A. Baykov, Sobraniye trudov [Collected Works], V, Izd. AN SSSR, 1948.

135. D.S. Belyankin and N.Ye. Filonenko, DAN SSSR, 2, 146 (1935).

136. P.P. Budnikov and Kh.S. Gevorkyan, Ogneupory, No. 7, 291 (1950).

137. A.S. Berezhnoy, Ogneupory, No. 6, 256 (1948); No. 8, 351 (1948).

138. G.V. Kukolev, Trudy 2-go soveshchaniya po ogneupornym materialam [Trans. of the Second Conference on Refractory Materials], 101, Izd. AN SSSR, 1941.

139. G.V. Kukolev and G.Z. Dolgina, Ogneupory, No. 12, 536 (1950).

140. G.V. Kukolev and M.A. Yalymova, Voprosy petrografii i mineralogii [Problems of Petrography and Mineralogy], 2, 256, Izd. AN SSSR, 1953.

141. W. Ostwald, Z. phys. Chem., 34, 493 (1900).

142. G.A. Hullet, Z. phys. Chem., 37, 385, 1905; J. Am. Chem. Soc., 27, 49, 1905.

143. H. Freundlich, Kapillarchemie [Capillary Chemistry], Leipzig, 1909.

144. M. Jones and J.R. Partington, J. Chem. Soc., 107 (2), 1019, 1915.

145. R. Gross, Jahrbuch. Radioakt. Electronik [Yearbook of Radioactive Electronics], 15, 270 (1918).

146. G.V. Kukolev and Ye.N. Leve, ZhPKh, 28, 807, 909 (1955)..

147. G.V. Kukolev and S.I. Shcheglov, Stat'ya v Sbornike trudov po khimii i tekhnologii silikatov [Articles in Collection of Works on Chemistry and the Technology of Silicates], 302, Promstroyizdat, 1957.

148. V.I. Danilov, Izv. AN SSSR, Seriya fiz., 5, No. 1, 30 (1941).

149. G.I. Taylor and H. Quinney, Proc. Roy. Soc., A143, 307 (1934); 163, 157 (1937).

150. G.W. Sears, J. Appl. Phys., 21, 721 (1950).

151. Dzh. Ye. Burke and D. Tarnball, Stat'ya v sb. I. Uspekhi fiziki metallov, perev. s angliyskogo pod red. Ya.S. Umanskogo and B.N. Finkel'shteyna [Articles in Collection I Entitled Progress in Metal Physics, Translation from the English Edited by Ya.S. Umanskiy and B.N. Finkel'shteyn], Metallurgizdat, Moscow, 1956.

152. J.S. Smart and A.A. Smith, Trans. Am. Min. Met. Eng., 152, 103 (1943).

153. L.I. Kogan and R.I. Entin, Problemy metallovedeniya i fiziki metallov [Problems of Metallurgy and Metal Physics], No. 2, 216, Metallurgizdat, 1951.

154. R. Karnop and G. Sachs, Z. Phys., 60, 464, 1930.

155. H.G. Mueller, Ztschr. Physik, 96, 279 (1935).

156. M. Kornfel'd and V. Pavlov, Phys., Z. Sowiet [Soviet Physics Journal], 6, 537 (1934); 12, 658 (1937); M. Kornfel'd, F. Savitskiy, ibid, 8, 528 (1935).

157. R.F. Mehl and J.K. Stanley, Trans. Am. Inst. Min. Met. Eng., 150, 260 (1942); R.F. Mehl, W.A. Anderson, ibid., 161, 140 (1945); J.K. Stanley, ibid. 162, 116 (1945).

158. A.A. Bochvar, ZhFP, 4, No. 1, 47 (1927).

159. A.A. Bochvar, Osnovy termicheskoy obrabotki splavov [Fundamentals of Heat Treatment of Alloys], Metallurgizdat, Moscow-Leningrad, 1940.

160. I.A.M. Limpt, St. v sb. Rekristallizatsiya metallov [Recrystallization of Metals], 148, Gosmashmetizdat [State Scientific and Technical Publishing House for Literature on Machinery and Metalworking], Moscow-Leningrad, 1933.

161. V.I. Danilov, Rasseyaniye rentgenovskikh luchey v zhidkostyakh [The Scattering of X-Rays in Liquids], ONTI, 1935.

162. V.I. Danilov, Stroyeniye i kristallizatsiya zhidkostey [The Structure and Crystallization of Fluids], Izd. AN SSSR, Kiev, 1956.

163. O.A. Yesin, Uspekhi khimii [Progress in Chemistry], 26, No. 12, 1374 (1957).

164. J.D. Bernal and R.H. Fowler, Trans. Farad. Soc., 29, 1049 (1933). J. Chem. Phys., 1, 515 (1933).

165. F.A. Lindemann, Phys. Ztschr, 11, 609 (1910).

166. W. Spring, Bull. Soc. Chem., 44, 166 (1885); 46, 209 (1886). z. phys. Chem., 2, 536 (1888).

167. D.S. Belyankin, N.A. Toropov and V.V. Lapin, Fiziko-khimicheskiye sistemy silikatnoy tekhnologii [Physicochemical Systems of Silicate Technology], Promstroyizdat, 1954.

168. A.S. Berezhnoy, Kremniy i yego binarnyye sistemy [Silicon and Its Binary Systems], Izd. AN SSSR, Kiev, 1958.

169. V. Ya. Anosov and S.A. Pogodin, Osnovnyye nachala fiziko-khimicheskogo analiza [Fundamental Principles of Physicochemical Analysis], Izd. AN SSSR, 1947.

170. N.S. Kurnakov, Vvedeniye v fiziko-khimicheskiy analiz [Introduction to Physicochemical Analysis], Izd. AN SSSR, Moscow, 1940;

Sobr. izbr. rabot [Collection of Selected Works], GONTI, Leningrad-Moscow, 1939.

171. P.P. Hall and H. Insley, J.Am. Ceram. Soc., 30, No. 11-12 (1947).

172. E.M. Levine, H.F. McMurdie and F.P. Hall, Phase Diagrams for Ceramics, Columbus, Ohio, 1956.

173. W.H.B. Roosebom, Z. phys. Chem., 30, 395 (1899); ZhRFKhO [Journal of the Russian Physicochemical Society], 33 (2), No. 6, 91 (1901).

174. V.M. Kravchenko, DAN SSSR, 79, No. 3, 443 (1951); 80, No. 6, 885 (1951); 82, No. 4, 597 (1952).

175. V.M. Kravchenko, ZhFKh, 27, No. 1, 6 (1953).

176. M.F. Shreder, Gornyy zhurnal [Mining Journal], No. 12, 272 (1890); Z. phys. Chem., 11, 449 (1893).

177. V.M. Kravchenko, ZhFKh, 13, 1523 (1939); 15, 652 (1941).

178. R. Becker, Proc. Phys. Soc., 52, 71 (1940).

179. R. Becker, Z.f. Metallkunde [Metallurgy Journal], 29, 245 (1937).

180. B.Ya. Pines, ZhETF, 13, No. 11-12, 411 (1943).

181. B.Ya. Pines, Izvestiya sektora fiz.-khim. analiza [Bulletin of the Department of Physicochemical Analysis], IONKh AN SSSR, 16, No. I, 65 (1943).

182. V.I. Danilov and D.S. Kamenetskaya, ZhFKh, 22, No. 1, 69 (1948).

183. D.S. Kamenetskaya, ZhFKh, 22, No. 1, 81 (1948).

184. D.S. Kamenetskaya, Stat'ya v sb. problemy metallovedeniya i fiziki metallov [Articles in Collection Entitled Problems of Metallurgy and the Physics of Metals], 113, 1949.

185. Ya.Ye. Geguzin and B.Ya. Pines, ZhTF, 23, 2078 (1953); DAN SSSR, 75, 387, 535 (1950).

186. Ya.Ye. Geguzin and B.Ye. Pines, DAN SSSR, 75, No. 4, 535 (1950).

187. B.M. Finkel'shteyn, St. v sb. Problemy metallovedeniya i fiziki metallov [Articles in Collection Entitled Problems of Metallurgy and Metal Physics], No. 3, 275, Metallurgizdat, Moscow, 1952.

188. I. Livshits, ZhETF, 9, 481 (1939).

189. L.S. Palatnik, DAN SSSR, 95, 1227 (1954).

190. L.S. Palatnik and V.M. Kantorovich, ZhFKh, 28, 1595 (1954).

191. L.S. Palatnik and A.I. Landau, ZhTF, 28, No. 10 (1958); Sb. trudov po khimii i tekhnologii silikatov, Promstroyizdat, 1957.

192. L.S. Palatnik and A.I. Landau, ZhFKh, 29, 1784, 2054 (1955); Uch. zapiski Khar'khovskogo gosuniversiteta [Scientific Reports of Kharkov State University], 71, 55, 1956.

193. L.S. Platnik and A.I. Landau, ZhFKh, 30, 2399, 1956; 31, 304 (1957); 31, 2739 (1957); DAN SSSR, 102, 125 (1955); 109, 954 (1956).

194. J.C. Maxwell, Collect Sci. Papers. Cambridge, 2, 625 (1890).

195. J. Stranski, Z. phys. Chem., 136, 259 (1928).

196. J. Stefan, Ann. Phys. u. Chemie [Annals of Physics and Chemistry], 17, No. 9, 550 (1882).

197. B.I. Sreznevskiy, ZhRFKhO, 15, No. 1, 1 (1883).

198. M. Thoma, Z. Phys., 64, 224 (1930).

199. W. Ostwald, Z. Phys. Chem., 34, 503 (1900).

200. H.W. Morse, Proc. of Am. Acad. Arts and Sciences, 45, 361 (1910).

201. L Langmuir, Phys. Rev., 12, 2, 368 (1918).

202. L.D. Landau, ZhETF, 7, 19, 627 (1937).

203. Ye.M. Livshits, ZhETF, 11, 255, 269 (1941); 14, 353 (1944).

204. G. Huettig, Z. angew. Chem. [Journal of Applied Chemistry], 49, 882 (1936).

205. G.F. Huettig, Z. anorg. allg. Chem. [Journal of Inorganic and General Chemistry], 224, 225 (1935); Z. Electrochem., 41, 429, 527 (1935).

206. N.B. Pilling and R.E. Bedworth, J. Inst. Metals, 29, 529 (1923).

207. F.C. Frank and J. van der Merwe, Proc. Roy. Soc. (A), 198, 203,

216 (1949) (A), 200, 125 (1950).

208. V. Zayt, Diffuziya v metallakh [Diffusion in Metals], IIL, Moscow, 1958.

209. J.A. Hedvall and J. Heuberger, Z. anorg. allg. Chem., 122, 181, 1922; 135, 49, 1924.

210. J.A. Hedvall, Z. anorg. allg. Chem., 128, 1 (1923); 140, 243 (1924); 154, 1 (1926); 162, 110 (1927).

211. G. Tamman, Z. anorg. allg. Chem., 149, 21 (1925).

213. G. Tamman, Z. anorg. allg. Chem., 135, 77 (1924); 160, 101 (1927).

214. J.A. Hedvall, Reaktionsfaehigkeit festen Stoffe [Reactivity of Solids], Leipzig, 1938.

215. J.A. Hedvall, Einfuehrung in die Festkoerperchemie [Introduction to Chemistry of Solids], Braunschweig, 1952.

216. C. Wagner, Z. phys. Chem., 34, 309 (1936); Z. anorg. allg. Chem., 236, 320 (1938).

217. C. Wagner, Trans. Farad. Soc., 34, 851 (1938).

218. W. Jost, Diffusion und chem. Reaction in festen stoffen [Diffusion and Chemical Reaction in Solids], Dresden, 1937.

219. W. Jander, Z. anorg. allg. Chem., 168, 113 (1927); 190, 65, 397 (1930); 191, 171 (1930); 192, 286 (1930).

220. W. Jander, K. Bunde, Z. anorg. Chem., 231, 345 (1937).

221. W. Jander, Z. anorg. allg. Chem., 163, 1 (1927).

222. W. Jander, Z. anorg. Chem., 49, 879 (1936).

223. R. Jagitsch et al., Arkiv. Kemi, Mineral., Geol., 15A, Vol. 6, No. 17, (1942); 22A, Vol. 2, Nos. 5, 6 (1946).

224. B. Bengston and R. Jagitsch, Arkiv Kemi, Mineral, Geol., 24A, Vol. 3, No. 18 (1947).

225. Cf. L'Etat solide. Rapports et discussions (9 Cons. de phys. a l'Univ. Brux) [Solid State. Reports and Discussions (9th Physics

Conference at the University of Brussels)], Brussels, 1952.

226. Cf. Proceed. International Symposium Reactivity of Solids. Vol. 1, 2, pp. 1, 195, 501, 619, 639, 683, 786, 801 et al., Gothenburg, 1954.

227. A.A. Baykov, Sbor. trudov [Collected Works], 2, 292, 318, 562, Izd. AN SSSR, 1948.

228. A.A. Baykov, Metallurg. [The Metallurgist], No. 3, 5 (1926).

229. D.Kh. Balarev and M.N. Nikolov, Reaktsii v tverdom sostoyanii [Reactions in the Solid State], Sofia, 1943.

230. P.P. Budnikov and A.M. Ginstling, Uspekhi khimii [Progress in Chemistry], 23, 491 (1954).

231. A.M. Ginstling and T.P. Fradkina, ZhPKh, 25, 1135, 1268 (1952).

232. C. Tubandt and H. Reinhold, Z. phys. Chem., 140, 291 (1929).

233. W.R. Foster, J. Am. Ceram. Soc., 34, 5, 151 (1951).

234. A.M. Ginstling, ZhPKh, 25, 277, 499 (1952).

235. D. Belarew, Z. anorg. allg. Chem., 136, 216 (1924); 138, 252 (1924); 143, 89 (1925); 153, 184 (1926); 160, 92 (1927).

236. M.Ye. Pozin and A.M. Ginstling, ZhPKh, 26, 561, 1953.

237. M.Ye. Pozin, A.M. Ginstling and V.V. Pechkovskiy, ZhPKh, 27, 376 (1954).

238. P.P. Budnikov and K.M. Shmukler, ZhPKh, 19, 1029 (1946).

239. P.P. Budnikov and Kh.O. Gevorkyan, ZhPKh, 24, 125 (1951).

240. P.S. Mamykin, Stat'ya v Sb. trudov, posvyashchennykh 60-letiyu P.P. Budnikova [Articles in a Collection of Works Devoted to the Sixtieth Anniversary of P.P. Budnikov], Promstroyizdat, 1946.

241. F. Taradoire, Rev. Chem. Ind. Mont. Sci. Quesneville [Review of Chemical Industry and Scientific Monitor of Quesneville], 47, 130, 169 (1938).

242. F. Taradoire, Bull. Soc. Chem. [Bulletin of the Chemical Society],

6, 866, 1249 (1939); 7, 720 (1940).

243. W. Jander, Z. anorg. allg. Chem., 174, 11 (1928).

244. A.N. Zelikman, Metallurgiya vol'frama i molibdena [The Metallurgy of Tungsten and Molybdenum], Metallurgizdat, 1949.

245. A.A. Babadzhan, Trudy instituta metallurgii Ural'skogo filiala AN SSSR [Trans. of the Metallurgy Institute of the Ural Branch of the Acad. Sci. USSR], No. 1, 74 (1957).

246. D.M. Chizhikov, Metallurgiya tyazhelykh tsvetnykh metallov [The Metallurgy of Heavy Nonferrous Metals], 89, 357, 649 et al., Izd. AN SSSR, Moscow-Leningrad, 1948.

247. V.Ya. Mostovich, Sb. trudov [Collected Works], I, 41, 65, 145, 167, 205, ONTI, Moscow-Leningrad, 1936.

248. V.I. Smirnov, Okislitel'nyy obzhig mednykh rud i kontsentratov [Oxidative Roasting of Copper Ores and Concentrates], ONTI, Sverdlovsk-Moscow, 1938.

249. P.G. Romankov, Gidravlicheskiye protsessy khimicheskoy tekhnologii [Hydraulic Processes of Chemical Engineering], Goskhimizdat, Leningrad-Moscow, 1958.

250. C. Wagner and W. Schottky, Z. phys. Chem., 11, 163 (1930); 22, 181 (1933); Z. phys. Chem., Bedenstein-Festband 177 (1931).

251. W. Schottky, Wiss. Veroeff. Siemens-Konzern, 14, N. 2, 1 (1935). Z. Elektrochem. angew. phys. Chem. 45, 33 (1939).

252. C. Wagner, Z. phys. Chem. 11, 139 (1930); 21, 25 (1933); 32, 447 (1936), 38, 295 (1937); Angew. Chem., 49, 735 (1936).

253. C. Wagner, Diffusion and High Temperature Oxidation of Metals, in Atom Movements, 153, Cleveland, 1951.

254. C. Tubandt, Handbuch d. Exper.-Physik [Experimental Physics Handbook], Vol. XII, 384, 394, 404, Leipzig (1932).

255. C. Tubandt and S. Eggert, Z. anorg. allg. Chem., 110, 196 (1920).

256. C. Tubandt, H. Reinhold and W. Jost, Z. phys. Chem., 129, 69 (1927); Z. anorg. Chem. 177, 253 (1928).

257. T. Burth and E. Posnjak, Z. Kristallogr. [J. Crystallogr], 82, 325 (1932).

258. O. Hagg and G. Soederholm, Z. phys. Chem., 29, 88, 95 (1935).

259. K. Hauffe, Stat'ya v sb. Uspekhi fiziki metallov [Article in Collection Entitled Progress in Metal Physics (Translation from Journal Entitled Progress in Metal Physics)], 1953, Gosmetallur-gizdat, Moscow, 1956.

260. K. Hauffe, Reaktionen in und an festen Stoffen [Reactions in and on Solids], Berlin, 1955.

261. R. Lindner, Arkiv Kemi, 5, No. 26, 277 (1953); Z. phys. Chem., 6, No. 3/4, 129 (1956).

262. V. Garner, Uspekhi khimii [Progress in Chemistry], 8, 1173 (1939); Science Progress, 33, 130, 209 (1938).

263. W.E. Garner and H.V. Pike, J. Ch. Soc. (L), 1565 (1937).

264. W.E. Garner and W.R. Southton, J. Ch. Soc. (L), 1705 (1935).

265. B.V. Yerofeyev, P.I. Bel'kevich and A.A. Volkova, ZhFKh, 20, 10, 1103 (1946).

266. Ye.S. Osinovik, Sb. nauchn. rab. In-ta khimii AN BSSR [Collection of Scientific Works of the Chemistry Institute of the Acad. Sci. of the Byelorussian Soviet Socialist Republic], No. 5 (1) (1956).

267. A. Wischin, Progr. Roy. Soc. A172, 314 (1936).

268. P.I. Bel'kevich, Dokt. dissertatsiya, Minsk (Minsk) (1950).

269. S.Z. Roginskiy and Ye.I. Shul'ts, Z. phys. Chem., A 138, 21 (1928).

270. B.V. Yerofeyev, Izvestiya AN BSSR [Bulletin of the Acad. Sci. Byelorussian Soviet Socialist Republic], No. 4, 137 (1950).

271. P.D. Dankov, Trudy soveshchaniya po voprosam korrozii [Trans. of

Conference on Problems of Corrosion], 139 (1938-1940).

272. P.D. Dankov and N.A. Shishakov, Izv. AN SSSR, ser. khim [Bulletin of the Acad. Sci. of the USSR, Chemical Series], No. 5-6, 1225 (1938); DAN SSSR, 24, 554 (1939).

273. N. Nelson, J. Chem. Phys., 5, 252 (1937).

274. D.A. Frank-Kamenetskiy, DAN SSSR [Proc. Acad. Sci. USSR], 23, 561 (1939).

275. P.D. Dankov, DAN SSSR, 23, 548 (1939).

276. P.D. Dankov, Izv. sekt. f.-kh analiza, AN SSSR [Bull. Sect. Physicochem. Anal. Acad. Sci. USSR], 16, 82 (1943).

277. T.M. Dyuko, Dissertatsiya, Sb. Tezisov dissertatsiy, zashchish-chennykh v LKhTI v 1935-1940 gg. [Dissertation, Collection of Theses of Dissertations Defended at the Leningrad Institute of Chemical Engineering for 1935-1940], 166, Leningrad (1941).

278. C. Wagner and E. Koch, Z. phys. Chem., 34, 317 (1936).

279. K. Hauffe, K. Pschera, Z. anorg. Chem., 262, 147 (1950).

280. P.V. Gel'd and O.A. Yesin, Protsessy vysokotemperaturnogo voss-tanovleniya [Processes of High-Temperature Reduction], Metallur-gizdat, 1957; P.V. Gel'd, Stal' [Steel], No. 7, 706 (1947).

281. P.V. Gel'd, M.I. Kochnev, A.G. Kologreyeva and N.N. Serebrennikov, ZhPKh, 21, 1250, 1261 (1948).

282. A.S. Mikulinskiy, ZhPKh, 24, 12, 42 (1951); Trudy Ural'skogo n.-i. khim. in-ta, No. 2, 3 (1954).

283. A.N. Vol'skiy, Osnovy teorii metallurgicheskikh plavok [Funda-mentals of the Theory of Melts], Metallurgizdat, 1943.

284. S.T. Rostovtsev, Teoriya metallurgicheskikh protsessov [Theory of Metallurgical Processes], Metallurgizdat, Moscow, 1956.

285. G. Tammann and A. Sworykin, Z. anorg. allg. Chem., 170, 62 (1928); ZhRFKhO, Part 2, No. 4, 257 (1928).

286. V.D. Ponomarev and I.R. Polyvyannyy, Izv. AN Kaz. SSR [Bulletin Acad. Sci. of the Kazakhstan SSR], ser. gorn. dela [Mining Series], No. 9, 3, 35 (1956).

287. V.I. Minayev, Izv. Tomskogo tekhnologicheskogo instituta [Bull. Tomsk Technological Institute], 44, 11 (1923).

288. P.P. Budnikov, DAN SSSR, 1, No. 6, 332 (1934); P.P. Budnikov and A.N. Sysoyev, Ukr. khim. zh. [Ukranian Chemical Journal], 4, No. 2, 113 (1928). P.P. Budnikov and M.I. Nekrich, Khim. prom. [Chem. Ind.], No. 7, 18 (1955).

289. S.K. Chirkov, Zh. khim. prom. [Journal of the Chemical Industry], 15, No. 6, 9 (1938).

290. S.N. Aall, Chem. Products, 8, 14 (1945).

291. F.S. Maron and A.S. Mikulinskiy, Sb. rabot UNIKhIMa Teoriya i praktika rudnoy elektrotermii [Collected Works of the Urals Chemical Scientific Research Institute for Chemistry and Metallurgy entitled Theory and Practice of Mining Electrothermics], 47 (1948).

292. A.S. Berezhnoy, ZhPKh, 13, 800 (1940).

293. I.G. Bubenin, Stroitel'nyye materialy [Structural Materials], No. 3, 3 (1937).

294. V.V. Lygina, Avtoreferat dissertatsii [Author's Abstract of Dissertation], LGU [Leningrad State University], Leningrad, 1954; Uch. zapiski Len. ped. in-ta im.A.I. Gertsena [Scientific Bulletins of the Leningrad Pedagogical Institute im. A.I. Gertsen], 117, 33 (1956).

295. W. Jander and J. Petri, Z. Electrochem., 44, 747 (1938).

296. P.P. Budnikov, A.S. Berezhnoy, I.A. Bulavin, B.M. Grissek, G.V. Kukclev and D.N. Poluboyarinov (Edited by P.P. Budnikov), Tekhnologiya keramiki i cgneuporov [The Technology of Ceramics and

Refractory Materials], Gosstroyizdat, Moscow, 1954.

297. I.I. Kitaygorodskiy, N.N. Kachalov, V.V. Vargin, K.S. Yevstrop'-
      yev and D.B. Ginzburg, Tekhnologiya stekla [The Technology of
      Glass], Promstroyizdat, Moscow, 1951.

298. J.H. Van't Hoff, Z. phys. Chem., 1, 165 (1887); 5, 352 (1890).

299. O.P. Mchedlov-Petrosyan, Stat'ya v sb. Fiziko-khimicheskiye osnovy
      keramiki [Article in Collection Entitled Physicochemical Bases of
      Ceramics], 499, Promstroyizdat, Moscow, 1956.

300. N.A. Landiya and O.P. Mchedlov-Petrosyan, Zapiski Vs. mineral.
      obshch. [Notes of the All-Union Mineralogical Society], Part 82,
      No. 3, 228 (1953).

301. V.A. Kireyev, ZhFKh, 22, 847 (1948), Sb. rabot po fizicheskoy
      khimii [Collection of Works on Physical Chemistry], AN SSSR,
      Moscow-Leningrad, 1947.

302. A.F. Kapustinskiy and K.B. Yatsimirskiy, ZhFKh, 22, 1271 (1948).

303. N.A. Landiya, ZhFKh, 25, 927 (1951); 27, 496, 624 (1953); Dokt.
      dissertatsiya [Doctorate Dissertation], IONKh AN SSSR, 1957.

304. S.A. Shchukarev, Uch. zapiski LGU, No. 79, No. 7, 197 (1945).

305. V.B. Glushkova, Zhurn. neorg. khim. [Journal of Inorganic Chemis-
      try], 2, 2438 (1957).

306. O.P. Mchedlov-Petrosyan, ZhFKh, 24, 1299 (1950).

307. N.A. Landiya and O.P. Mchedlov-Petrosyan, ZhFKh, 26, 1785 (1952).

308. A.I. Avgustinik and O.P. Mchedlov-Petrosyan, ZhFKh, 26, 1785
      (1952); O.P. Mtschedlov-Petrossian and W.J. Babuschkin, Silikat-
      technik [Silicate Technology], 9, No. 5, 209 (1958).

309. W. Jander and J. Wuhrer, Z. anorg. Chem., 266, 225 (1936).

310. A.I. Avgustinik, P.Z. Tandura, L.I. Sverchkova, ZhPKh, 22, 1150
      (1949).

311. K.S. Kutateladze and V.I. Lutsenko, Ogneupory [Refractory Mater-

ials], No. 11, 499 (1949).

312. W. Trzebiatowski, J. Damm and T. Romotowski, Rocznici Chem. [Chemistry Yearbook], 30, 431 (1956).

313. V.M. Kakabadze and G.D. Chachanidze, Trudy Gruz. politekhn. in-ta [Trans. of the Georgian Polytechnical Institute], No. 28, 3, 110 (1953); ZhPKh, 25, 1013 (1954).

314. E.K. Keler and V.B. Glushkova, Zhurn. neorg. khim., 1, 2283 (1956); 2, 1001 (1957).

315. G.M. Matveyev, Stat'ya v Sb. trudov po khim. i tekhnol. silikatov [Article in Collection of Papers on the Chemistry and Technology of Silicates], Promstroyizdat, Moscow, 1957; Izv. Vyssh. uch. zaved. MVO SSSR, Khimiya i khim. tekhnologiya [Bulletin of the Higher Educational Institutions of the Ministry of Higher Education of the USSR, Chemistry and Chemical Engineering], 1, No. 2, 135 (1958).

316. N.A. Toropov, Khimiya tsementov [The Chemistry of Cements], Promstroyizdat, 1956.

317. P.P. Budnikov, Gips [Gypsum], Moscow, Stroyizdat, 1943.

318. I. Zawadzki, Przeglad Chem. [Chemical Review], R.S., No. 11-12, 239 (1947).

319. V.R. Terashkevich and G.N. Yevetskiy, ZhPKh, 9, 2155 (1936).

320. S.M. Royak, M.I. Gershman, K.F. Miloslavskiy and Z.I. Negerova, Trudy VNIITs, No. 10, 5-121 (1935).

321. "TAPPI", 39, No. 6, 353 (1956).

322. R. Schenck and K. Jordan, Z. anorg. allg. Chem., 178, 4, 389 (1929).

323. S. Weychert and I. Leyko, Przemysl Chem., 12 (35), No. 5, 258 (1956).

324. A.D. Volkov, Trudy Leningradskogo tekhnologich. in-ta [Trans. of the Leningrad Technological Institute], No. 7 (1958); A.M.

Ginstling and A.D. Volkov, ZhPKh, 33, 1700 (1960).

325. E.V. Britske, A.F. Kapustinskiy, B.K. Veselovskiy, L.M. Shamovskiy, L.G. Chentsova and B.I. Anvayer, Termicheskiye konstanty neorganicheskikh veshchestv [Thermal Constants of Inorganic Substances], Izd. AN SSSR, Moscow, 1949.

326. R. Benner, Termokhimicheskiye raschety [Thermochemical Calculations], IIL, Moscow, 1950.

327. F.D. Rossini, Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Stand. Circ. 500, 1952.

328. M.I. Temkin and L.A. Shvartsman, Uspekhi khimii [Progress in Chemistry], 17, No. 2 (1948).

329. L.P. Vladimirov, Uskoreniye metody termodinamicheskikh raschetov ravnovesiya khimicheskikh reaktsiy [The Acceleration of Methods of Thermodynamic Calculations of the Equilibrium of Chemical Reactions], Izd. L'vovskogo gos. universiteta [Publishing House of the L'vov State University], 1956.

330. W. Jander, Angew. Chem., 41, 79 (1928).

331. G. Tammann, Z. anorg. allg. Chem., 111, 78 (1920); 122, 27 (1922).

332. G. Tammann and W. Koester, Z. anorg. allg. Chem., 123, 196 (1922).

333. W. Jander, Z. anorg. allg. Chem., 166, 31 (1927).

334. W. Jander, Z. anorg. allg. Chem., 202, 135 (1931).

335. P.S. Mamykin and S.G. Zlatkin, ZhFKh, 9, No. 3, 393 (1937).

336. V.F. Zhuravlev, I.G. Lesokhin and R.G. Tempel'man, ZhPKh, 21, 887 (1948).

337. G.R. Pole and N.W. Taylor, J. Am. Ceram. Soc., 18, 325 (1935).

338. J. Guillissen and R. Rysselberghe, Trans. Am. Electrochem. Soc. 59, 95 (1931).

339. I.T. Howarth, W. Maskill and W.E.S. Turner, J. Soc. Glass Techn., 17, 25, T (1933).

340. R. Jagitsch and J.A. Hedvall, Arkiv Kemi, Miner., Geol., 19, A, No. 14, 1 (1945).

341. K. Fischbeck and W. Jellinghaus, Z. anorg. allg. Chem., 165, 55, (1927).

342. F. Bischoff, Z. anorg. allg. Chem., 250, No. 10, 22 (1942).

343. I.S. Lileyev, Trudy GIPKh [State Institute of Applied Chemistry], No. 28, 26 (1936); Khimiya i tekhnologiya okisi alyuminiya [Chemistry and Technology of Aluminum Oxide], part 1, 1940.

344. W. Jander and E. Hoffman, Angew. Chem. [Applied Chemistry], 46, 76 (1933); Z. anorg. Chem., 218, 211 (1934).

345. A.I. Avgustinik and O.K. Kurdevanidze, ZhPKh, 19, 1189 (1946).

346. A.M. Ginstling, ZhPKh, 25, 718 (1952).

347. M. Volmer, Kinetik der Phasenbildung [The Kinetics of Phase Formation], Leipzig, 1939.

348. A.A. Bochvar, Issledovaniye mekhanizma i kinetiki kristallizatsii splavov evtekticheskogo tipa [Investigation of the Mechanism and Kinetics of the Crystallization of Eutectic-Type Alloys], ONTI, Moscow-Leningrad, 1935.

349. B. Topley and J. Hume, Proc. Roy. Soc., A 120, 211 (1928).

350. G. Huettig and E. Lehmann, Z. phys. Chem., B 19, 420 (1932).

351. B.V. Yerofeyev, DAN SSSR, 52, 515 (1946).

352. B.V. Yerofeyev and N.I. Mitskevich, Sb. nauchn. rabot. In-ta khimii AN BSSR, No. 5, (1), 3 (1956).

353. P.I. Bel'kevich, A.A. Volkova and B.V. Yerofeyev, Izv. AN BSSR, No. 6, 145 (1948); No. 5, 145 (1950).

354. V.P. Korniyenko, Uch. Zapiski Khar'kovsk. gos. universiteta, Trudy n.-issl. in-ta khimii i khim. fakul't. [Scientific Notes of the Khar'kov State University, Trans. of Scientific Research Institute of Chemistry and the Chemistry Faculty], 11, 21, 27

(1954).

355. B.V. Yerofeyev and I.I. Smirnov, ZhFKh, 26, 1233 (1952).

356. B.V. Yerofeyev and N.I. Mitskevich, ZhFKh, 24, 1285 (1950); 26, 848, 1631 (1952); 27, 118 (1953).

357. P.I. Bel'kevich, Sb. nauchn. rabot In-ta khimii AN BSSR, No. 5 (1), 21 (1956).

358. R.S. Bradley, J. Colvine, J. Hume, Philos. Mag., 14, 1102 (1932); Proc. Roy. Soc., A 137, 531 (1932).

359. S. Roginsky, Sow. Phys., 1, 640 (1933).

360. S.V. Ismailow, Sow. Phys., 4, 835 (1933).

361. B.V. Yerofeyev, ZhFKh, 9, 828 (1937).

362. O.M. Todes and R.I. Bogutskiy, ZhETF, 11, 133 (1941); 12, 79 (1942).

363. O.M. Todes, ZhFKh, 14, 1224 (1940).

364. O.M. Todes, Sb. rabot po fizich. khimii [Collected Works on Physical Chemistry], 154, Izd. AN SSSR, Moscow-Leningrad, 1947.

365. K. Mampel, Z. phys. Chem., A 187, 43, 235 (1940).

366. B.V. Yerofeyev and V.A. Protashchik, Sb. nauchnykh rabot In-ta khimii AN BSSR, No. 5 (1), 58, 75 (1956).

367. A.M. Ginstling and B.I. Brounshteyn, ZhPKh, 23, 1249 (1950).

368. O.A. Yesin and P.V. Gel'd, Fizicheskaya khimiya pirometallurgich-eskikh protsessov [The Physical Chemistry of Pyrometallurgical Processes], Metallurgizdat, I, 1948; II, 1954.

369. N.A. Toropov, A.M. Ginstling and I.G. Luginina, DAN SSSR, 84, No. 2, 293 (1952).

370. M.S. Fadeyeva, Dissertatsiya, Len. tekhnol. in-t im. Lensoveta [Dissertation, Leningrad Technology Inst. im. Leningrad Soviet], 1952.

371. I.G. Luginina, ZhFKh, 29, 1873 (1956).

372. T.D. Averbukh, M.A. Serebrennikova and N.D. Maslova, Trudy Ural'skogo n.-issl. khim. in-ta, No. 1, 3 (1954).

373. D. Cismaru, Studii Cercet. Fiz. Acad. R.P.R., 6, No. 3, 435 (1955).

374. D. Cismaru, Studii si cercetarichim, 5, No. 1, 119 (1957).

375. B. Stalhane, Jernkontorest annaler, No. 3, 95 (1929). B. Stalhane and T. Malmberg, ibid., No. I,1,(1930); No. 12, 609 (1930).

376. W. Jander, Z. angew. Chem., 41, 73 (1928).

377. M. Mueller, Chem. Fabrik [Chemical Plant], 32, 333 (1933).

378. A.N. Vol'skiy, Teoriya metallurgicheskikh protsessov [Theory of Metallurgical Processes], ONTI, Moscow-Leningrad, 1935.

379. M.A. Pavlov, Metallurgiya chuguna [Metallurgy of Cast Iron], 1, Metallurgizdat, Moscow, 1945.

380. B.S. Gulyanitskiy and D.M. Chizhikov, Izv. AN SSSR, OTN, No. 11, 13 (1955).

381. S.Z. Roginskiy, ZhFKh, 12, 427 (1938).

382. G. Huettig, Koll. Z., 94, No. 2, 137 (1941); No. 3, 258 (1941).

383. M.Ye. Pozin and A.M. Ginstling, ZhPKh, 23, 37 (1950).

384. P.P. Budnikov and A.S. Berezhnoy, ZhPKh, 13, 1277 (1940).

385. P.P. Budnikov and A.S. Berezhnoy, Uspekhi khimii, 15, No. 5, 521 (1946); 17, No. 5, 585 (1948).

386. P.P. Budnikov and L.G. Gulinova, Stat'ya v sb. Novoye v stroitel'-noy tekhnike (red. S.P. Nichiporenko), Kiev, Ak. arkh. USSR [Articles in Collection Entitled Innovations in Building Technique (Edited by S.P. Nichiporenko), Kiev, Academy of Architecture of the Ukranian Soviet Socialist Republic], 1953.

387. C.C. Furnas, Bur. Mines Bull., 307 (1929); Ind. Eng. Chem., 22, No. 1, 26, No. 7, 721 (1930).

388. A. Anzelius, Z. angew. Math. u. Mech., 6, No. 4 (1929).

389. B.I. Kitayev, Teploobmen v shakhtnykh pechakh [Heat Transfer in

Shaft Furnaces], Metallurgizdat, Sverdlovsk, 1945.

390. B.N. Vetrov and O.M. Todes, ZhTF, 25, 1217, 1232, 1242 (1955).

391. A.M. Ginstling, Stat'ya v Sb. trudov, posvyashchennykh 70-letiyu
P.P. Budnikova [Article in Collected Papers Devoted to the Seven-
tieth Birthday of P.P. Budnikov],Promstroyizdat, Moscow, 1956.

392. M.I. Strelkov, Stat'ya v Sb. trudov, posvyashchennykh 60-letiyu
P.P. Budnikova [Article in Collected Works Devoted to the Sixtieth
Birthday of P.P. Budnikov], BTI MPSM [Bureau of Technical Infor-
mation, Ministry of the Structural Materials Industry], 1946.

393. B.I. Brounshteyn and A.M. Ginstling, ZhPKh, 29, 1870 (1956).

394. P.P. Budnikov and L.G. Gulinova, ZhPKh, 9, 1937 (1936).

395. A.S. Berezhnoy, Stat'ya v Sb. trudov, posvyashchennykh 60-letiyu
P.P. Budnikova, Promstroyizdat, Moscow, 1946.

396. I.S. Kaynarskiy and N.A. Sidorov, ZhPKh, 29, 1785 (1956).

397. A.S. Berezhnoy, Dokt. dissertatsiya, In-t metallurgii AN SSSR,
1946.

398. A.M. Ginstling, Dokt. dissertatsiya, Leningr. Tekhnol. in-t im.
Lensoveta, 1954.

399. J.T. Howarth, W.E.S. Turner, J. Soc. Glass. Techn., 14, 402 (1930).

400. V.I. Lutsenko, Kinetika obrazovaniya silikatov magniya v tverdoy
faze [Kinetics of the Formation of Magnesium Silicates in Solid
Phase], Kand. dissertatsiya, Gruz. politekhn. in-t im. S.M.
Kirova [Candidate's Dissertation, Georgian Polytechnic Inst. im.
S.M. Kirov], Tbilisi, 1949.

401. A.M. Ginstling and M.I. Muratova, ZhPKh, 26, 640 (1953).

402. P.P. Budnikov and A.M. Ginstling, Ukr. khim. zh. [Ukrainian Chem.
J.], 21, 109 (1955).

403. L.I. Karyakin and I.S. Kaynarskiy, DAN SSSR,70, No. 6, 1049 (1950);
81, No. 5, 887 (1951); 86, No. 1, 137 (1952).

404. I.S. Kaynarskiy and E.V. Degtyareva, DAN SSSR, 91, No. 2, 355
(1953); 99, No. 2, 301 (1954).

405. A. Simon, F. Thuemmler, E. Kluegel, Proc. Int. sympos. react.
solids, I, 163, Gothenburg, 1954.

406. I.I. Kitaygorodskiy, Ogneupory, No. 12, 15 (1946).

407. D.N. Poluboyarinov and V.L. Balkevich, Ogneupory, No. 12, 583
(1949); No. 3, 109 (1951).

408. M. Ye. Pozin and A.M. Ginstling, ZhKhP [Journal of the Chemical
Industry], No. 9, 259 (1950); Trudy Leningr. tekhnol. in-ta im.
Lensoveta, No. 20, 16 (1951).

409. N.A. Toropov and I.G. Luginina, Tsement [Cement], No. 1, 4; No. 2,
17 (1953).

410. J.A. Hedvall, A. Eldh, Z. anorg. allg. Chem., 226, 192 (1936).

411. M.O. Kharmadar'yan and G.V. Marchenko, Ukr. khim. zh., 8, No. 1,
95 (1933).

412. G. Tammann, O. Mansuri, Z. anorg. allg. Chem., 126, 119 (1923).

413. E. Kordes, Z. anorg. allg. Chem., 149, 67 (1925).

414. S.G. Tresvyatskiy and A.M. Cherepanov (Ed. P.P. Budnikov), Vysoko-
ogneupornyye materialy i izdeliya iz okislov [High-Refractory
Materials and Objects Made of Oxides], Gosmetallurgizdat, Moscow,
1957.

415. W.E. Kingston (Ed.), Physics of Powder Metallurgy, New York, 1951,
article by C.G. Goetzel.

416. P. Murray, E.P. Rodgers, A.E. Williams, Trans. Brit. Ceram. Soc.,
53, 474 (1954).

417. L.G. Berg, O.K. Yanat'yeva and B.M. Savitskiy, DAN SSSR, 75, No.
3, 383 (1950).

418. Ya.V. Klyucharov and S.A. Levenshteyn, Paper in collection en-
titled Fizikokhimicheskiye osnovy keramiki [Physicochemical

Fundamentals of Ceramics], Promstroyizdat, 1956.

419. G.G. Tsurinov, Pirometr N.S. Kurnakova [Pyrometer of N.S. Kurnakov], Izd. AN SSSR, Moscow, 1953.

420. H. Le Chatelier, Compt. rend. Acad. sci., 108, 1046 (1889).

421. D.S. Belyankin and K.M. Feodot'yev, Zap. Vs. miner. ob-va [Notes of the All-Union Mineralogical Society], series 2, part 80, No. 1, 88 (1951).

422. E.K. Keler and A.K. Kuznetsov, Dokl. AN SSSR, 88, No. 6, 1031 (1953).

423. E.K. Keler and A.K. Kuznetsov, Trudy I soveshch. po termografii [Trans. of the First Conf. on Thermography], p. 239, Izd. AN SSSR, 1955; ZhNKh, 1 1292 (1956).

424. A.I. Kitaygorodskiy, Rentgenostrukturnyy analiz melkokristallicheskikh i amorfnykh tel [X-Ray Structural Analysis of Fine-Crystalline and Amorphous Solids], Izd. tekhn.-teor. lit., Moscow-Leningrad, 1952.

425. I.B. Borovskiy, Fizicheskiye osnovy rentgenospektral'nykh issledovaniy [Physical Bases of X-Ray Spectral Investigations], Izd. MGU, Moscow, 1956.

426. Ya.S. Umanskiy, A.K. Trapeznikov and A.I. Kitaygorodskiy, Rentgenografiya [Roentgenography], Mashgiz, 1951.

427. N.A. Toropov, P.F. Konovalov, A.I. Yefremov, G.V. Anan'yeva, Tsement, No. 3, 17 (1954).

428. P.F. Konovalov and A.I. Yefremov, Trudy soveshchaniya po khimii tsementov [Trans. of Conference on the Chemistry of Cements], Promstroyizdat, 1956.

429. D.S. Belyankin and V.P. Petrov, Kristalloptika [Crystal Optics], Gosgeolizdat, Moscow, 1951.

430. G.B. Bokiy, Immersionnyy metod [Immersion Method], Izd. AN SSSR,

- 548 -

1950. K./II ... CI ICK, 95, No. 2, 355

431. A.I. Brodskiy, Khimiya izotopov [The Chemistry of Isotopes], Izd. AN SSSR, 1952.

432. V.I. Veksler, L.V. Groshev and B.M. Isayev, Ionizatsionnyye metody issledovaniya izlucheniy [Ionization Methods in Radiation Research], Izd. tekhn.-teor. lit., 1950.

433. B. Rossi and G. Shtaub, Ionizatsionnyye kamery i schetchiki [Ionization Chambers and Counters], IIL, 1951.

434. W. Jonson, Trans. Am. Inst. Min. Met. Eng., 143, 107 (1941).

435. A. Val' and N. Bonner (Ed.), Ispol'zovaniye radioakrivnosti pri khimicheskikh issledovaniyakh [The Use of Radioactivity in Chemical Research], IIL, 1954.

436. C.N. Fenner, J. Wash. Acad. Sci., 2, 471 (1912); Am. J. Sci., 36, 331 (1913).

437. N.N. Sinel'nikov, DAN SSSR, 92, No. 2, 369 (1953); 102, No. 3, 555 (1955); 110, No. 4, 651 (1956); 106, No. 5, 870 (1956); ZhNKh, I, No. 10, 2409 (1956).

438. R. B. Sosman, Trans. Brit. Ceram. Soc., 54, 655 (1955).

439. O.W. Floerke, Ber Dtsch. Ker Ges. [Reports German Ceramic Society], 32, 369 (1955).

440. R.W. Grimshaw et al., Trans. Brit. Ceram. Soc., 47, 269 (1948); 55, 36 (1956).

441. T. Tokuda, J. Ceram. Assoc. Japan., 63, No. 715, 582, 589 (1955).

442. H. Schurete and H. Stollenwerk, Arch. Eisenhuettenwesen [Archives of Iron Metallurgy], 26, No. 10, 583 (1955).

443. N.A. Sazhin and Ye.A. Pepelyayeva, Doklad na mezhdunarodnoy konferentsii po mirnomu ispol'zovaniyu atomnoy energii [Report at International Congress on Peaceful Uses of Atomic Energy], Izd.

AN SSSR, 1955.

444. A.S. Berezhnoy and L.I. Karyakin, Ogneupory, No. 3, 111, No. 5, 211 (1952).

445. O. Ruff and F. Ebert, Z. anorg. allg. Chem., 180, 19 (1929).

446. E. Ryschkewitsch, Oxydkeramik der Einstoffsysteme von Standpunkt der Phys. Chemie [Oxide Ceramics of Single-Component Systems From the Standpoint of Physical Chemistry], Berlin, Gottingen, Heidelberg, 1948.

447. A. Dietzel and H. Tober, Ber. Deut. Ceram. Ges., 30, No. 3, 47; No. 4, 71 (1953).

448. W. Cohn, S. Tolksdorf, Z. phys. Chem., 8, 331 (1930).

449. R.F. Geller, P.J. Javorsky, Journ. Res., 35, No. 1, 87 (1945).

450. C.C.E. Curtis, J. Amer. Ceram. Soc., 30, No. 6, 180 (1947).

451. P. Duwez, F.H. Brown, F. Odell, J. Amer. Ceram. Soc., 33, 274 (1950); 35, 107 (1952); J. Electrochem. Soc., 98, 356 (1951).

452. A.J. Green, G.H. Stewart, Ceramics, A Symposium, London, 1953.

453. E.K. Keler and N.A. Godina, Ogneupory, No. 9, 416 (1953).

454. A.I. Belyayev, Metallurgiya legkikh metallov [The Metallurgy of Light Metals], Metallurgizdat, Moscow, 1954.

455. V.A. Mazel', Proizvodstvo glinozema [The Production of Alumina], Metallurgizdat, Moscow, 1955.

456. L.Ya. Markovskiy, D.L. Orshanskiy, V.P. Pryanishnikov, Khimicheskaya elektrotermiya [Chemical Electrothermy], GKhI [State Chem. Lit. Press], Leningrad-Moscow, 1952.

457. S.K. Popov, Izvestiya AN SSSR, ser. fizich., 10, 505 (1946).

458. D.S. Belyankin, Trudy In-ta geol. nauk. AN SSSR, 106, No. 30, 1 (1949).

459. Ed. A.V. Shubnikov, Trudy In-ta Kristallogr. AN SSSR, 8 (1953).

460. N.A. Toropov, DAN SSSR 1, No. 2-3, 147 (1935); Trudy tret'yego

soveshchaniya po eksperimental'noy mineralogii i petrografii [Trans. of the Third Conference on Experimental Mineralogy and Petrography], Izd. AN SSSR, 211 (1940).

461. N.A. Toropov and M.M. Stukalov, DAN SSSR, 24, No. 5, 458 (1939); 27, No. 9, 974 (1940).

462. N.A. Toropov and F.Ya. Galakhov, Sb., posvyashchennyy akad. D.S. Belyankinu [Collection Devoted to Academician D.S. Belyankin], Izd. AN SSSR, 1946.

463. D.S. Belyankin, V.V. Lapin and Yu.P. Simanov, Izv. AN SSSR, OTN [Div. Tech. Sci.], No. 4, 561 (1946).

464. D.N. Poluboyarinov, Ogneupory, No. 8, 353 (1952); D.N. Poluboyarinov, R.Ya. Popil'skiy and A.A. Mayer, Trudy MKhTI imeni Mendeleyeva [Moscow Institute of Chemical Technology (im. D.I. Mendeleyev)], No. 19, 133 (1954).

465. J.W. Greig, E. Posnjak, H.E. Merwin, R.B. Sosman, J.Am. Science, 30, No. 5, 239 (1935).

466. B.N. Dolgov, Kataliz v organicheskoy khimii [Catalysis in Organic Chemistry], GKhI, Moscow, 1959.

467. T.E. Bradborn, G.R. Rigby, Trans. Brit. Ceram. Soc., 52, 417 (1953).

468. W.T. Wilde, W.J. Rees, Trans. Brit. Ceram. Soc., 42, 123 (1943).

469. G.H. Lovel, G.R. Rigby, A.T. Green, Iron Steel Inst. Sp. Rep., 32, 81 (1946).

470. G.R. Rigby, in Ceramics, A Symposium, p. 488, London, 1953.

471. A.N. Winchell, Amer. mineral., 26, 412 (1941).

472. I.R. Rait, Iron Steel Inst. Sp. Rep., 31, 182 (1945).

473. G.H.B. Lovell, Trans. Brit. Ceram. Soc., 50, No. 8, 315 (1951).

474. G.A. Rankin, H.E. Merwin, J. Am. Chem. Soc., 38, 571 (1916); Z. anorg. Chem., 96, 294 (1916).

475. A.S. Bazilevich, Min. syr'ye [Mineral Raw Materials], No. 9, 25 (1934); Trudy VIOK [All-Union Scientific Research Institute of Fireproof and Acid-Resistant Materials], 6, 17 (1936).

476. A.S. Berezhnoy and Ye.Z. Slonimskiy, Tr. Khar'kovsk. in-ta ogneuporov [Trans. of the Khar'kov Institute of Refractory Materials], 45, 78 (1939).

477. A.S. Berezhnoy and V.M. Tsynkina, Sb. materialov po voprosam ogneupornoy promyshlennosti [Collection of Data on Problems of the Refractory Materials Industry], No. 2, 38, Metallurgizdat (1940).

478. E.S. Dana, W.E. Ford, A Textbook of Mineralogy, New York, 1943.

479. I.A. Morozevich, Opyty nad obrazovaniyem mineralov v magme [Experiments on the Formation of Minerals in the Magma], Warsaw, 1897.

480. P.K. Chirvinskiy, Iskusstvennoye polucheniye mineralov v XIX stoletii [Synthetic Derivation of Minerals in the Nineteenth Century], Kiev, 1903-1905.

481. J.A. Hedvall, Z. anorg. allg. Chem., 92, 301 (1915).

482. J.A. Hedvall, J. Heuberger, Z. anorg. allg. Chem., 116, 137 (1921).

483. O. Krause, W. Tiel, Ber. Deutsch. Keram. Ges., 104, 169 (1934).

484. V. Ya. Mostovich and G.S. Uspenskiy, Tsvetnyye metally [Nonferrous Metals], No. 7, 960 (1930).

485. P.P. Budnikov, V.G. Avetikov, Ye.I. Dudavskiy and A.L. Zvyagil'-skiy, DAN SSSR, 68, No. 2, 313 (1949).

486. W. P. Foster, H.F. Royal, J. Am. Ceram. Soc., 32, No. 1, 26 (1949).

487. F.Ya. Galakhov, Izv. AN SSSR, OKhN, No. 5, 525 (1957); No. 9, 1032 (1957).

488. S.M. Lang, R.S. Roth, C.L. Fillmore, J. Res. Nat., 53, 201 (1954).

489. H. Forestier, M. Galand, Compt. rend., 193, 733 (1931).

490. S. Hilpert, A. Wielle, Z. phys. Chem., 18, 291 (1932).

491. G. Huettig, D. Zinker, H. Kittel, Z. Electrochem., 40, 306 (1934).

492. G. Huettig, G. Sieber, H. Kittel, Acta Physiochim. URSS, 2, 139 (1935).

493. E. Jenkel, Z. anorg. Chem., 220, 377 (1934).

494. P.I. Yudinson, Kh.S. Nikogosyan and N.L. Dilaktorskiy, Ogneupory, No. 1, 33 (1933).

495. Kh.S. Nikogosyan, Mineral'noye syr'ye [Mineral Raw Materials], No. 7, 728 (1931).

496. Kh.S. Nikogosyan and N.L. Dilaktorskiy, Mineral'noye syr'ye, No. 2-3, 20 (1932).

497. K.M. Feodot'yev and D.A. Vogman, Trudy 2-go soveshch. po eksp. miner. i petrogr. [Trans. of the Second Conference on Exp. Min. and Petrogr.], Izd. AN SSSR, Moscow, 1937.

498. W. Jander, H. Pfister, Z. anorg. Chem., 239, 95 (1938).

499. P. Lipinski, Tonind.-Ztg., 67, 139 (1943).

500. R.L. Pevzner, DAN SSSR, 55, No. 3, 237 (1947).

501. S.G. Tumanov, DAN SSSR, 57, No. 1, 69 (1947).

502. J.A. Hedvall, V. Ny, Z. anorg. Chem., 235, 148 (1937).

503. G. Huettig, H. Kittel, Z. anorg. Chem., 217, 194 (1934).

504. N.L. Dilaktorskiy and A.A. Kadenskiy, Trudy 3-go soveshch. po eksp. miner. i petrogr., Izd. AN SSSR, 217 (1940).

505. K. Fischbeck, E. Einecke, Z. anorg. Chem., 167, 32 (1927).

506. W. Jander, W. Stamm, Z. anorg. Chem., 199, 167 (1931).

507. P.P. Budnikov and A.S. Berezhnoy, Dopov. AN USSR, No. 5, 345 (1950)

508. B.Ya. Pines and Ye.I. Ter-Mikaelyants, Trudy Ukr. in-ta ogneuporov, 37, 5 (1936).

509. T.Ye. Krasenskaya, Ya.N. Yasinovskiy and V.V. Goncharov, Ogneupory, No. 5-6, 329 (1940).

510. D.S. Belyankin and N.M. Chervinskiy, Trudy Petrografichskogo in-ta

No. 13, 214 (1938).

511. A.S. Berezhnoy, DAN SSSR, 53, No. 1, 49 (1946).

512. W. Rüedorff, B. Reuter, Z. anorg. Chem., 253, 194 (1947).

513. K. Lagerqvist, S. Wallmark, A. Westgren, Z. anorg. Chem., 234, 1
    (1937).

514. M.S. Novakovskiy and L.I. Ponirovskaya, Uch. zapiski Khar'kovsk.
    gos. universiteta, 30, 256, X (1950); 14, X (1956).

515. L.I. Ponirovskaya, Dissertatsiya, Khar'k. gos. universiteta
    [Dissertation. Kharkov State University], 1958.

516. R. Jagitsch. Chem. Ztbl., 2, 1296 (1936).

517. V.N. Yung and Yu.M. Butt, Tsement [Cement], No. 7, 29 (1938).

518. N.Ye. Filonenko, DAN SSSR, 64, 529 (1949).

519. E. Dufau, Compt. rend, 121, 689 (1895).

520. P.P. Budnikov, Ogneupory, No. 11-12, 25 (1945); DAN SSSR, 51, 8,
    615 (1946).

521. V.F. Zhuravlev, Trudy Leningr. khim.-tekhnol. in-ta [Trans. of the
    Leningrad Chemical Engineering Institute], 7, 211 (1939).

522. F.I. Basenin, ZhPKh, 12, 651 (1939).

523. J. Konarzewski, Rocz. Chem., 11, 516, 607 (1931).

524. H. Forestier, Compt. rend. 192, 842 (1931).

525. R. Nacken, M. Gruenewald, Zement, 15, 615 (1926).

526. S. Nagai, K. Asaoka, J. Soc. Chem. Ind. (Jap.) 33, 130B (1930).

527. S. Nagai, T. Joshiura, J. Soc. Chem. Ind (Jap.), 38, 374B (1935).

528. J. Hedvall, S. Sandberg, Z. anorg. Chem., 240, 15 (1938).

529. D.S. Belyankin, N.A. Toropov and T.M. Dyuko, Trudy in-ta tsem.
    [Trans. of the Cement Institute], No. 18, 57 (1937).

530. N.A. Toropov, DAN SSSR, 23, 74 (1939).

531. H. Forestier, G. Chaudron, Compt. rend., 181, 509 (1925).

532. H. Forestier, Ann. Chem., 9, 368, 375, 388 (1928).

533. S. Hilpert, A. Lindner, Z. phys. Chem., 22, 395 (1933).

534. R.S. Hilpert, R. Schweinhagen, Z. phys. Chem., 31, 1 (1935).

535. N.A. Toropov, DAN SSSR, 1, 147 (1935).

536. G. Grube, G. Heintz, Z. Electrochem, 41, 797 (1935).

537. S. Wallmark, A. Westgren, Arkiv Kemi, Miner., Geol., 12B, 35
(1937); Ceram. Abstr., 24, 46 (1945).

538. A.I. Avgustinik and O.P. Mchedlov-Petrosyan, ZhPKh, 20, 584, 1125
(1947).

539. A.N. Morozov, Metallurg., No. 1, 15 (1939).

540. M. Erchak, I. Fankuchen, R. Ward, J. Amer. Soc. Chem., 68, 2085
(1946).

541. M.Ye. Pozin and A.M. Ginstling, ZhPKh, 23, 1149, 1245 (1950); 24,
134 (1951).

542. G. Natta, L. Passerini, Gazz. Chim. Ital., 60, 389, 754 (1930).

543. E. Kohlmeyer, Met. u. Erz. N15-16, 447, 483 (1913).

544. H. Strassen, Z. Electrochem., 41, 476 (1935).

545. H. Hauptmann, J.Novak, Z. phys. Chem., 15, 365 (1931).

546. K. Hild, Z. phys. Chem., (A) 161, 305 (1932).

547. H. Kittel, Z. anorg. Chem., 222, 1 (1935).

548. H. Kittel, Z. anorg. Chem., 221, 49 (1934).

549. R. Geller, E. Bunting, J. Res. Nat. Bur. St., 31, 255 (1943).

550. R. Hay, J. White, A. McIntosh, J. West. Scot. Iron and St. Inst.,
42, 99 (1934-35); J. Amer. Ceram. Soc., N2, part 2, 97 (1947).

551. A. McIntosh, J. Rait, R. Hay, J. Roy. Techn. Coll., 4, 72(1937);
J. Amer. Ceram. Soc., 21, 119 (1938).

552. W.A. Fischer, A. Hoffmann, Naturwiss., 41, 162 (1954).

553. G. Lovell, G. Rigby, A. Green, Trans. Brit. Cer. Soc., 46, 200
(1947).

554. V.V. Goncharov and A.T. Kleynberg, Zap. Vseross. miner. o-va

[Bulletins of the All-Russian Mineralogical Society], 68, 199 (1939).

555. V.V. Goncharov, K.M. Feodot'yev and D.A. Vogman, Ogneupory, No. 9, 552 (1936).

556. S. Zerfoss, H. Davis, J. Amer. Cer. Soc., 29, 15 (1946).

557. J.A. Hedvall, L. Leffler, Z. anorg. allg. Chem., 234, 235 (1937).

558. H.R. Thirsk, E.J. Whitmore, Trans. Farad. Soc., 36, 862 (1940).

559. J.A. Hedvall, N.V. Zweigbergk, K. Vet. Akad. (Stockholm), Ark. Kemi, 7, No. 20 (1919).

560. W. Pucall, Silikatz, 2, 65, 87, 109 (1919).

561. H. Wartenberg, E. Prophet, Z. anorg. Chem., 208, 369 (1932).

562. I.P. Baytkus, Dissertatsiya, In-t khimii silikatov AN SSSR, Leningrad, 1956; E.G. Keler and N.B. Karpenko, ZhNKh, 4, 1125 (1959).

563. M.G. Harwood, H.A. Klasens, Nature, 165, 73 (1950).

564. L.D. Yershov, Trudy Giprotsementa [State Institute for the Design and Planning of Establishments and for Scientific Research in the Cement Industry], No. 1, 5 (1940).

565. L. Parga-Pondal, Tonn-Industrie-Ztg, No. 83, 85 (1933).

566. J.A. Hedvall, K. Andersson, Scient. papers Inst. Phys. Chem. Research, 38, 210, Tokyo (1941).

567. A. Bergstein, Chem. listy, 50, No. 1, 3 (1956).

568. P. Crepax, G. Gottardi, Atti Ist. veneto sci. Lettere ed arti. Cl. sci. nat. e natur, 113, 69 (1954-1955).

569. Y. Tanaka, J. Chem. Soc. Japan, 62, 199 (1941); Bull. Chem. Soc. Japan, 16, 428 (1941); 17, 70, 186 (1942).

570. S. Tamaru, N. Ando, Z. anorg. allg. Chem., 184, 385 (1929); 195, 309 (1931); J. Chem. Soc. Japan, 52, 36, 107 (1931).

571. F. Ebert, E. Cohn, Z. anorg. Chem., 213, 321 (1933).

572. W. Jander, G. Lorenz, Z. anorg. Chem., 248, 105 (1941).

573. G. Tammann, W. Oelsen, Z. anorg. Chem., 193, 245 (1930).

574. F.N. Strokov et al. Trudy GIPKh, No. 32, 4-25, 41-95 (1940).

575. G. Gibson, R. Ward, J. Am. Ceram. Soc., 26, 130 (1943).

576. M.D. Beals, S. Zerfass, J. Am. Ceram. Soc., 27, 285 (1944).

577. P.P. Budnikov and M.A. Matveyev, DAN SSSR, 107, No. 4, 547 (1956).

578. C. Kroeger, W. Greaser, Z. anorg. Chem., 242, 393 (1939).

579. I.I. Kitaygorodskiy, Steklo i steklovareniye [Glass and Glass-making], 178-180, Promstroyizdat, Moscow, 1950.

580. I.I. Kitaygorodskiy and Ya.A. Shkol'nikov, Tekhn. otchet In-ta stekla [Technological Report of the Glass Institute], 1934.

581. J.A. Hedvall, G. Schiller, Z. anorg. Chem., 221, 97 (1934).

582. R.A. Morgan, P.A. Hummel, J. Am. Ceram. Soc., 32, No. 8, 250 (1949).

583. F. Machatschki, Z. phys. Chem., 133, 253 (1928).

584. P.P. Budnikov and A.M. Cherepanov, DAN SSSR, 74, No. 5, 1011 (1950).

585. J.A. Hedvall, Z. anorg. Chem., 98, 57 (1916).

586. H. Haraldsen, Zentralbl. Mineral., Abt. A. 9, 297 (1928).

587. E. Thilo, G. Rodde, Ber. Deut. Chem. Ges., 72, 34 (1939).

588. H. Thurnauer, A.R. Rodriguez, J. Am. Ceram. Soc., 25, 445 (1942).

589. H. Haraldsen, Neues Jahrbuch Min., 61. Abt. A 139 (1930).

590. W. Eitel, Ber Deut. Keram. Ges., 24, 37 (1943).

591. S. Nagai, J. Soc. Chem. Ind. (Japan), 34, 471 (1931); 35, 10, 161, 370 (1932); 36, 264, 326 (1933); 37, 303, 419, 549 (1934); 38, 229, 294 (1935).

592. J. Sanada, J. Soc. Chem. Ind. (Japan), 41, (1), 10 (1938).

593. S. Nakashev and K. Kazanovich, Trudy Vs. in-ta tsementov, 18, 36 (1937).

594. J. Konarzewsky, Przemysl. Chem., 16, 165 (1932).

595. R. Jagitsch, Sitzber. Akad. Wiss. (Wien) Math. Naturw. Klasse,
11 (b) 145, 221 (1936).

596. W. Maskill, G.H. Whiting, W.E.S. Turner, J. Soc. Glass. Techn.,
16, 94 (1932).

597. P.P. Budnikov and D.P. Bobrovnik, Ukr. Khim. zh. [Ukrainian Chemis-
try Journal], 12, book 4 (1937); Trudy tret'yego soveshchaniya po
eksper.miner. and petrografii, Izd. AN SSSR, Moscow-Leningrad,
223 (1940).

598. S. Kondon et al., J. Jap. Cer. Ass., 40 (447), 559 (1932).

599. S. Kondon et al., J. Jap. Cer. Ass., 43 (509), 273 (1935).

600. J. Hedvall, Glasstechn. Ber., 20, 34 (1942).

601. H. A. Bredig, J. phys. Chem., 48, 747 (1943).

602. K. T. Greene, J. Res. Nat. Bur. Stand., 32, 1 (1944).

603. D.S. Belyankin and V.V. Lapin, DAN SSSR, 51, No. 9, 707 (1946).

604. A. Valkenburg, H. McMurdie, J. Res. Nat. Bur. Stand., 38, 415
(1947).

605. N.A. Toropov and P.F. Konovalov, DAN SSSR, 30, No. 9, 663 (1938);
40, No. 4, 178 (1943).

606. C. Midgley, Acta Crystallographica, 5, 307 (1952).

607. N.A. Toropov, B.V. Volkonskiy and V.I. Sadkov, DAN SSSR, 112, No.
3, 467 (1957).

608. P. Eskola, Am. J. Sci. (F.s.), 4, 331, 345 (1922).

609. R.W. Nurse, J. Appl. Chem., 2, 244 (1952).

610. E.K. Keler, and V.B. Glushkova, ZhPKh, 30, 517 (1957).

611. N.L. Bowen, J. Wash. Acad. Sci., 8, 265 (1918); J. Amer. Ceram.
Soc., 2, 261 (1919).

612. H. F. Krause, W. Weyl, Z. anorg. Chem., 163, 355 (1927).

613. G. Grube, R. Truchesess, Z. anorg. Chem., 208, 75 (1931).

614. A. Pabst, Z. phys. Chem., A142, 227 (1929).

615. A. Karl, Compt. rend., 194, 1743 (1932).

616. W. Jander, H. Richl, Z. anorg. Chem., 246, 81 (1941).

617. J.A. Hedvall, P. Sjaman, Z. Electrochem., 37, 130 (1931).

618. N.A. Toropov and F.Ya. Galakhov, DAN SSSR, 78, No. 2, 299 (1951); Izv. AN SSSR, OKhN, No. 1, 8 (1958).

619. F. Ya. Galakhov, Dokt. dissertatsiya, In-t khimii silikatov [Doctorate Dissertation, Inst. of Silicate Chemistry], AN SSSR, Leningrad, 1959.

620. P.P. Budnikov, S.G. Tresvyatskiy, V.I. Kushakovskiy, DAN SSSR, 93, No. 2, 281 (1953).

621. J. Jakob. Schweiz. Min. Petr. Mitt., 20, 8 (1940); Ceram. Abs., 47 (1942).

622. J. Greig, J. Amer. Ceram. Soc., 8, No. 8, 365 (1925).

623. T. Ao, J. Soc. Chem. Ind. (Jap.), 36 (10), 546 (1933).

624. P.P. Budnikov, DAN SSSR, 49, No. 3, 205 (1945).

625. J.W. Hyslop, H.P. Rooksby, Trans. Ceram. Soc. (Engl.), 27, 93 (1927/28).

626. W. Keyser, Ber. Dtsch. ceram. Ges., 21, 29 (1940).

627. C. Matington, Comp. rend., 177, No. 24, 1290 (1923).

628. V.H. Stott, A. Hilliard, Trans. Brit. Ceram. Soc., 48, No. 4, 133 (1949).

629. N.A. Zhirnova, Iz laboratoriy In-ta keramiki [From Laboratories of Inst. of Ceramics], No. 45, 31, Gizlegprom [State Scientific and Technical Publishing House of the Ministry of Manufactured Consumer Goods], Leningrad, 1934.

630. N.J. Kreidl, J. Amer. Ceram. Soc., 25, N 5, 129 (1942).

631. J.T. Howarth, R. Sykes, W.E.S. Turner, J. Soc. Glass. Techn., 18, 290 (1934).

632. N.W. Taylor, F.J. Williams, Bull. Geol. Soc. Am., 45 (7), 1121 (1935).

633. H.E. Ehrenberg, Zentralbl. Miner., 5, 129 (1932).

634. H. Strassen, Zement, 25, 218 (1936).

635. J. Phemister, R.W. Nurze, F.A. Baunister, Miner. Mag., 26, 225 (1942).

636. E. Thilo, Z. Krist., 101, 345 (1939).

637. A. Bystroem, Svensk Kem. Tid., 54, 10 (1942).

638. P.P. Budnikov, V.G. Avetikov and A.A. Zvyagil'skiy, DAN SSSR, 81, No. 5, 883 (1951).

639. L. Gjessing, Norsk. Geol. Tid., 20, 265 (1941).

640. G. Jager, DRP N 615696.

641. V.M. Tsynkina, Tekhnologiya tsirkoniyevykh ogneuporov, Vs. in-t ogneuporov [Technology of Zirconium Refractory Materials. All-Union Inst. of Refractory Materials], Collection of papers on silicates, Publishing House of the Ministry of Building Materials RSFSR, Moscow, 1946.

642. P.R. Poole, Chem. Eng. Min. Rev., 31 (366), 250 (1939).

643. E.I. Krech, ZhPKh, 10, 1930 (1937).

644. P.P. Budnikov, Z. angew. Chem., 5, 8 (1923).

645. G. Tammann, C.F. Grevemeyer, Z. anorg. Chem., 136, 114 (1924).

646. P.P. Budnikov and A.N. Sysoyev, ZhPKh, 13, 719 (1940); P.P. Budnikov, Izbrannyye trudy [Selected Works], Izd. AN USSR, 443, Kiev, 1960.

647. P.P. Budnikov, Trudy 3-go Vs. soveshch. po ogneuporn. materialam [Trans. of the Third All-Union Conference on Refractory Materials], Izd. AN SSSR, 1947.

648. P.P. Budnikov and V.I. Khramova, DAN SSSR, 84, No. 2, 325 (1952); Ukr. khim. zh., 20, 447 (1954).

649. R. Rieke, E. Voelker, Ber. Dtsch. keram. Ges., 11, 608 (1930).

650. N.P. Bogoroditskiy and I.D. Fridberg, Elektrichestvo [Electricity], No. 5, 72 (1958).

651. N.P. Bogoroditskiy and I.D. Fridberg, Elektrofizicheskiye osnovy vysokochastotnoy keramiki [Electrophysical Bases of High-Frequency Ceramics], Gosenergoizdat, Moscow-Leningrad, 1958.

652. S.D. Okorokov, Vzaimodeystviye mineralov portlandtsementnogo klinkera v protsesse tverdeniya tsementa [Reaction of Minerals of Portland-Cement Clinker in the Setting Process of Cement], Stroyizdat, Moscow-Leningrad, 1945.

653. R.H. Bogue, Chemistry of Portland Cement, New York, 1947.

654. H. Kuehl, Zement-Chimie., 1, 2, Berlin, 1951, 1958.

655. E.M. Lea, F.M. Desch, Chemistry of cement and concrete, London, 1956.

656. V.N. Yung, Osnovy tekhnologii vyazhushchikh veshchestv [Fundamentals of the Technology of Cementing Substances], Promstroyizdat, Moscow, 1951.

657. R.E. Simanovskaya and S.Ya. Shpunt et al., Gips i fosfogips [Gypsum and Phosphogypsum], Sborn. rabot. NIUIF pod red. S.I. Vol'fkovicha [Collected Works of the Scientific Institute of Fertilizers and Insectifuges (im Ya.V. Samoylov)], Edited by S.I. Vol'fkovich, No. 160 (1958).

658. A.M. Ginstling and A.D. Volkov, ZhPKh, 32, 2171 (1959); 33, 274 (1960); 33, 736 (1960).

659. P.P. Budnikov and A.F. Cherkasova, DAN SSSR, 102, No. 4, 793 (1955).

660. P.P. Budnikov and R.D. Azelitskaya, DAN SSSR, 108, No. 3, 515 (1956).

661. V.N. Yung and V.V. Timashev, Tsement, No. 4, 4 (1956); No. 1, 4 (1957).

- 561 -

662. V.V. Timashev, Trudy MKhTI imeni D.I. Mendeleyeva, No. 24, 69 (1957).

663. Yu.M. Butt and V.V. Timashev, Khim. nauka i promyshlennosti, 3, No. 1, 14 (1958).

664. V.N. Yung, Yu.M. Butt, V.V. Timashev, ZhPKh, 30, 1298 (1957).

665. P.P. Budnikov and O.M. Sologubova, DAN SSSR, 85, No. 5, 1127 (1952).

666. M.I. Strelkov, Byull. tekhn. informatsiya Yuzhgiprotsementa [Bulletin of Technological Information of the Southern State Institute for the Design and Planning of Enterprises and Scientific Research in the Cement Industry], No. 1 (22), 1 (1957).

667. R.H. Bogue, Solid-phase reactions in the manufacture of Portland cement. Int. Symposium React. of Solids. Gotenburg, 1952; Nat. Bur. Stand. Pap. No. 65, 1952.

668. W. Bussem, H.E. Schweite, Tonind. Ztg., 56, 801 (1932).

669. W.C. Hansen, L.T. Brownmiller, R.H. Bogue, J.Am. Chem. Soc., 50, 396 (1928).

670. H.F. McMurdie, J. Res. Nat. Bur. Stand., 18, 475 (1937).

671. M.A. Swayze, Am. J. Sci., 244, 1, 65 (1946).

672. N.A. Toropov, L.D. Merkov and N.A. Shishakov, Tsement, No. 1, 28 (1937).

673. N.A. Toropov and A.I. Boykov, Izv. AN SSSR, OKhN, No. 6, 972 (1955).

674. S.D. Makashev, Trudy Giprotsementa, No. 2, 3 (1940).

675. S.M. Royak, Trudy NIITsementa [Trans. of the State All-Union Scientific Research Institute of the Cement Industry], No. 2, 3, Promstroyizdat, 1949.

676. S.D. Makashev, Tsement, No. 4, 3 (1950).

677. N.A. Toropov and S.L. Vol'fson, Tsement, No. 4, 12 (1953).

- 562 -

678. R.D. Azelitskaya, Tsement, No. 3, 13 (1953).

679. S.D. Okorokov and S.L. Golynko-Vol'fson, B.I. Sheveleva and
T.N. Yarkina, Tsement, No. 3, 5 (1957); No. 1, 16 (1958).

680. A.M. Paley, Tsement, No. 3, 5 (1957); No. 4, 23 (1958).

681. W.I. Satarin, Cement, Wapno, Gips, 14, No. 4, 83 (1958).

- 563 -

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